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IN ENGLISH TRANSLATION

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JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

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EVALUATION OF THE RESULTS OF SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSIS BY MEANS OF POISSON'S DISTRIBUTION

V. V. Nalimov and V. V. Nedler

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Evaluation of analytical results on the basis of errors calculated by some means or other, is only possible when the law governing the distribution of these errors is known. The errors of quantitative spectrographic analysis expressed in percentage concentration, or as the logarithms of the line intensity, usually conform to normal distribution [1-6]. In this case the square error is calculated. Using the law of normal distribution, and knowing the size of the error, it is easy to establish the probability of the appearance of experimental results with deviations not exceeding some given limit.

TABLE 1

Semi-Quantitative Determination of W

Range of error, in parts of σ	Absolute frequencies			
	Expected for a Gaussian distribution		Actually found	
0,0 —0,67	72,4		80	
0,67—1,0	27,1		19	
1,0 —1,4	22,8		6	
1,4 —2,0	16,9		0	
2,0 —2,6	5,3	6,7	26	41
2,6 —3,0	1,0		12	
>3,0	0,4		3*	

c=0,01—0,05%.

*Two errors had the value 9σ.

Evaluation of the accuracy of semi-quantitative spectrographic analysis is considerably more complicated; this analytical technique is very widely used in geological-prospecting work (metallometric surveys, preliminary sorting of geological test samples, etc.). Annually in the USSR several millions of such analyses are carried out by various geological-prospecting organizations.

The results of semi-quantitative spectrographic analysis are usually presented by means of a specially developed scale of discrete values. For example, when a test material contains 0.01% of some material, then according to a scale corresponding to a three-stage concentration range, the results can be represented by a series of discrete results: 0.01, 0.03, 0.1, 0.003, and 0.001% etc. The discrete nature of the analytical results, and the large error involved, which is comparable to the mean value of the analytical results, indicate that we cannot expect a normal distribution for the analytical results. As an example, in Table 1 a comparison is made of the experimentally established distribution of errors for the semi-quantitative analysis of tungsten, and the expected distribution based on a Gaussian distribution. It is quite obvious from Table 1 that there is not even an approximate agreement between the distribution actually observed and normal distribution. Calculations of the criteria of agreement gave, in this instance, the following results: $\chi^2 \approx 208$ for three degrees of freedom; $P(> \chi^2)$ 0.00001. Among 146 determinations there were two samples with errors of 9σ. These errors cannot be discarded as spurious, since they have also been observed during the determination of other elements, although their appearance would be excluded in practice, were the distribution of errors to conform to a normal distribution. A similar disagreement between the expected frequencies and those actually found has also been observed during the semi-quantitative determination of other elements.

The idea behind using one error or another for evaluating the experimental results is, that by using one cipher, the large amount of experimental material which has been obtained during the study of errors can be ciphered. Such a compilation of information can only be carried out when the law of the distribution of errors is known – this is the key by means of which this information can be interpreted in future. In the case under discussion – the semi-quantitative determination of tungsten and other elements – the distribution of errors is still unknown; accordingly, calculation of the square error is of no metrological significance. Knowing this value, it is impossible to forecast the frequency of the appearance of one particular deviation or another. It is doubtful in this case whether two square errors obtained in various laboratories characterize the quality of the work in these laboratories, since in such a case the factual material which is ciphered by these errors remains unknown.

A normal distribution might be expected according to the central limiting theorem of Liapunov, since the effect of a number of random factors distributed arbitrarily, under conditions where there are no factors which are greater than the majority of the remaining factors, is added up. In information theory, on the basis of the concept of entropy as a measure of the scattering of random values, it is shown that the normal distribution is the most random distribution of all possible distributions. In quantitative spectrographic analysis, analytical methods are usually developed so that the factors which determine the appearance of errors are excluded – by automatically fulfilling the requirements which are an outcome of the central limiting theorem of Liapunov – accordingly, a distribution approximating to a normal distribution is obtained [6]. A normal distribution, generally speaking, is a distribution of continuous values. Nevertheless, in practical work, all the results of measurements, including those of chemical determinations, are discrete to some extent or other, in the first instance because the results of measurements can only be obtained as a multiple of the smallest unit which the instrument used for measuring is capable of, and, secondly, in view of rounding off which is always adopted during calculation. During quantitative analysis, the extent of this discreteness is less than the observed changes in the value being measured, accordingly, one can with a fair degree of approximation ignore this factor, and regard x as a continuous value. The position is totally different in the case of semi-quantitative analysis: the coarse scale of evaluation has an essential effect on the distribution of the analytical results – this effect therefore becomes the dominating factor. In a random normal distribution the element of arbitrary randomness is introduced – the distribution of values becomes essentially discrete. As a result of this, the conditions for the appearance of a normal distribution, which is a consequence of the Liapunov theorem, are destroyed. In this case, on the basis of formal mathematical considerations, we might expect a Poisson distribution, which may be regarded as a special limiting case of a normal distribution [7], on which is superimposed the limitation indicated above imposed by the use of a coarse measuring scale which quantizes the experimental results.

Let us consider the following case. During styloscopic analysis, the elements are determined by comparing the intensity of two analytical lines. Here, we are dealing with a coarse measuring scale, which is determined by the number of pairs of lines with equal intensity in a given concentration range, since the human eye can only contrast the equality of two intensities. If the styloscope should be provided with a special photometric setup by means of which the line intensity can be changed uniformly, then we would get a fairly fine measuring scale, by means of which it would be possible to change over from discrete semi-quantitative analysis to continuous quantitative analysis.

Thus, on the basis of general metrological considerations, it is possible to give the following fairly strict classification of analytical methods:

1) Quantitative analysis – this is a method in which the results of repeated, successive determinations of the same value form a practically continuous collection of values. The degree of discreteness which is introduced by the measuring scale of the apparatus, rounding off during calculation, etc., is not the dominating factor in the general balance of errors. The values of the errors differ by one order or more from the content being determined.

2) Semi-quantitative Analysis – this is a method in which the results of repeated, successive determinations form a discrete succession of values, while the degree of discreteness (the value of the interval between two possible determinations) is of the same order of magnitude as the value being determined.

3) Qualitative Analysis – this is a special case of semi-quantitative analysis, where the results of a determination are mutually exclusive: the element is either present or not.

In order to present the results of semi-quantitative analysis in the form of a Poisson distribution, we shall use a special code consisting of a series of whole, positive numbers: 0, 1, 2, 3 . . . Let us assume that we have a

TABLE 2

Semi-Quantitative Determination of W, Mo, Sb, Cu, Bi, Zn, Pb, and Ag

	Absolute frequencies															
	W 0,01–0,03%		Mo 0,003–0,01%		Sb 0,01–0,10%		Cu 0,03–1,00%		Bi 0,003–0,01%		Zn 0,03–0,50%		Pb 0,01–0,50%		Ag 0,001–0,003	
	Expected acc. to the poisson distr.	Actually found experimentally	Expected acc. to the Poisson distr.	Actually found experimentally	Expected acc. to the Poisson distr.	Actually found experimentally	Expected acc. to the Poisson distr.	Actually found experimentally	Expected acc. to the Poisson distr.	Actually found experimentally	Expected acc. to the Poisson distr.	Actually found experimentally	Expected acc. to the Poisson distr.	Actually found experimentally	Expected acc. to the poisson distr.	Actually found experimentally
0	97,6	92	88,2	81	52,9	47	98,4	97	61,2	53	68,4	61	26,7	24	11,5	10
1	39,2	49	45,7	57	35,5	44	39,4	43	33,8	48	42,7	53	21,6	26	13,2	16
2	7,8	5	11,9	10	11,9	11	7,9	7	9,3	5	13,1	13	8,8	7	7,4	5
3	1,0	0	1,8	0	2,6	1	1,0	0	1,7	0	2,4	0	2,3	3	2,8	5
4	0,1	0	0,2	0	0,3	0	0,1	0	0,2	0	0,3	0	0,4	0	0,8	0
λ	0,40		0,52		0,67		0,39		0,55		0,62		0,81		1,14	
σ^2/λ	0,77		0,75		0,73		0,86		0,62		0,72		0,86		0,86	
$P(>\chi^2)$	$\sim$0,04		$\approx$0,04		$\approx$0,07		$\approx$0,3		$\approx$0,001		$\approx$0,05		$\approx$0,2		$\approx$0,3	
$P(<\chi^2/(l-1))$	$\approx$0,02		$\approx$0,01		$\approx$0,02		$\approx$0,05		$\approx$0,001		$\approx$0,01		$\approx$0,25		$\approx$0,3	

sample containing 0.01% of some element or other, and that we carry out determinations using the threefold concentration scale. The following results might be obtained during repeated determinations: 1) c = 0.01%, in this case, the determination has been carried out without error and the results can be coded by the number 0; 2) c = = 0.03% or c = 0.003% – the experimental results fall into the nearest concentration range (to the right or left of the true content) and the error can be coded by the number 1; 3) c = 0.1% or c = 0.001% – the experimental results fall within the second concentration range, the error can be coded by the number 2, etc. For repeated determinations we would get a series of numbers:

$$002010230000102\ldots. \qquad (1)$$

One often comes up against the presentation of experimental material by means of a series of numbers (1) in applied problems in the theory of probability. Let us assume that in a certain region T there are N points. The question may arise: what is the probability of finding m points in region t which is part of T? In the same way, for example, it is possible to formulate the problem which arises during a study of the distribution of structural components on a macrosection by means of a measuring grid. In this case the results of measurements of the number of nodules of a certain structural component falling within one measuring cell or another, are expressed by a series of numbers. If the points in region T are distributed randomly and independently of each other, it can be shown that the Poisson distribution is fulfilled [8]:

$$P_\lambda(m) = \frac{\lambda^m e^{-\lambda}}{m!}, \qquad (2)$$

where λ is the mean number of points in region t (the mean arithmetic series of numbers (1)); m = 0, 1, 2..., $P_\lambda(m)$ is the probability that m points fall within the region t being measured. If the Poisson distribution is strictly observed, it is easy to show that $\sigma^2 = \lambda$.

In semi-quantitative analysis the multitude of determinations can be regarded as a continuous sequence of equal intervals t, while to each determination there corresponds some number of a series (1) which characterizes one error or another of the determination.*

Poissson's law, generally speaking, is only fulfilled when the probability of the appearance of an event in the short interval Δt, is proportional to Δt, and events appear independently of each other [9]. The parameter of the Poisson distribution can be represented by the expression: $\lambda = kt$, where t is interpreted as some measure of the section in which the event appears; $k = N/T$ is the average number of events appearing in unit measure. In semi-quantitative analysis, the probability of the appearance of an error is inversely proportional to the chosen multiplicity of the concentration scale. Accordingly, in our case, the interval t should be regarded as some arbitrary measure, by means of which the concentration of the test material in the sample is expressed, and this measure can assume the values $^1/_3$, $^1/_2$, $^1/_{1.5}$ etc. according to whether 3, 2, or 1.5-fold intervals for the concentration scale are chosen for analysis. Poisson's law can be written in the form:

$$P_{kt}(m) = \frac{(kt)^m e^{-kt}}{m!}. \qquad (3)$$

If in any series of experiments with a measure t_1 an accuracy of $\sigma^2 = \lambda$ is achieved, then using the relation $\lambda = kt$, it is possible to achieve accuracy for another measure t_2 (for a concentration scale with another multiplicity).

Table 2 contains results obtained by treating material obtained during a study of the accuracy of semi-quantitative spectrographic analysis of synthetic standards with known amounts of the test elements. The standards were prepared on the basis of the following compounds: 1) SiO_2; 2) $SiO_2 + CaCO_3$ in the ratio 1 : 1; 3) $SiO_2 + FeS_2$ 3 : 1; 4) $SiO_2 + CaCO_3 + MgO$ 3 : 2 : 1; 5) $SiO_2 + Na_2CO_3$ '3 : 1; 6) $SiO_2 + Al_2O_3$ 3 : 1; 7) $SiO_2 + CaCO_3 +$ + MgO 4 : 1 : 1; 8) SiO_2 + pyrites 4 : 1. The analysis was carried out by blowing the test material with a stream

*In Poisson's distribution, m = 0, 1, 2, 3 . . . is an arithmetic progression, while in our case the concentration intervals increase in geometric progression. This circumstance should not lead to any perplexity, since the value actually measured ΔS is proportional to the logarithm of the concentration, while on a logarithmic scale we shall have an arithmetic progression.

of air between the carbon electrodes of an A.C. arc [10]. Each standard was analyzed 10-15 times, using a scale with $t = 1/3$. The experimental error for samples differing in composition were combined in one collection of numbers of type (1). For example, when we had two standards with contents of 0.03 and 0.01%, and on analysis we found 0.03% in both cases, then, for the first sample this result was coded by the number 0, while the second was coded by the number 1, etc. Table 3 contains results obtained by treating 797 analyses of niobium in geological samples. For spectrograms taken on the same plate, determination was carried out both semi-quantitatively (using a scale with $t = 1/2$), and quantitatively by using a microphotometer and a calibration curve. Comparison of the results obtained by both the methods indicated was carried out by means of a series of numbers similar to series (1).

TABLE 3

Semi-Quantitative Determination of Nb

m	Absolute frequencies	
	Expected from Poisson distr.	Actually found
0	424,5	399
1	267,4	309
2	84,4	74
3	17,7	14
4	2,8	1
5	0,4	0
λ	0,63	
σ^2/λ	0,86	
$P(>\chi^2)$	0,004	
$P(<\chi^2/(l-1))$	0,002	

It follows from an examination of the tabulated results that the frequency distribution of the results obtained experimentally is in fairly good agreement with the distribution to be expected from a Poisson distribution. It is interesting to note that the large errors ($m = 2$; $m = 3$) which are unavoidable during semi-quantitative determinations occur with frequencies which agree quite well with the frequencies expected from a Poisson distribution.

In order to make an absolutely objective evaluation of the probability of the deviation between experimental and calculated frequencies, criteria of agreement were calculated:

1) We determined the weighted sum of the squares.

$$\chi^2 = \sum_{i=1}^{s} \frac{(n_i' - n_i)^2}{n_i'}. \tag{4}$$

where $n_1 n_2 \ldots n_s$ is the experimental series of frequencies; $n'_1 n'_2 \ldots n'_s$ the theoretical series of frequencies calculated on the basis of (2) in which the value λ found for the experimental series is substituted; s is the number of frequencies in the series. The sum found (4) is distributed approximately like χ^2 with $s-2$ degrees of freedom when all the values $n'_i \geq 5$ (when certain groups do not satisfy this condition they are combined).

2) We determined the value [9]:

$$\chi^2 (l-1) \approx \frac{\sum_{i=1}^{l} (x_i - \lambda)^2}{(l-1)\lambda} = \frac{\sigma^2}{\lambda} \tag{5}$$

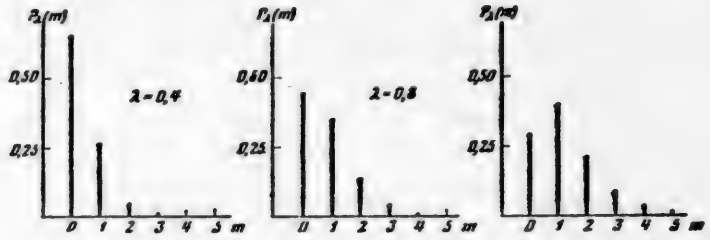
where $x_1 x_2 \ldots x_l$ is the series of values obtained by us corresponding to series (1). The distribution $\chi^2/(l-1)$ is tabulated in [11] right up to large values of $(l-1)$.

Results for the calculations* of the criteria of agreement are given in the lower columns of Tables 2 and 3. We see that in most cases $P(>\chi^2) \geq 0.04$, while in three cases this value is > 0.20; all this testifies to the accuracy of our hypothesis regarding the agreement between the experimental frequencies and Poissons's law. The ratio σ^2/λ proved to be always less than unity, this decrease being almost invariably within reasonable limits, since, in almost all cases, the probability $P(<\chi^2/(l-1) \geq 0.01$, while in three cases it was even considerably greater than 0.05. In our case, naturally, one cannot count on such good agreement between experimental and theoretical

* All the calculations in Tables 1, 2, and 3 were rounded off considerably.

results, as is possible, for example, during the study of electron emission from a cathode when additional non--random factors are completely excluded. In semi-quantitative spectrographic analysis, already in view of its limited sensitivity, in a number of cases there may occur non-random deviations between the experimental results and Poisson's law. For example, if we analyze a sample with a low content of test material, the appearance of a much higher result is by no means restricted, while the appearance of much lower results is restricted by the sensitivity limits of the method – all results below a certain limit will be expressed as "traces" , coding by one cipher. Accordingly, for samples with a low content of test material, the number of determinations with indices m - 3, m - 4 may be lower than what would be expected on the basis of a Poisson distribution – this circumstance lowers the value σ considerably; accordingly, in some cases, σ^2/λ will be appreciably less than unity.

Thus, the errors of semi-quantitative spectrographic determinations, generally speaking, conform to a Poisson distribution,* although deviations from this law are possible in certain cases. In each case, we can affirm that the experimentally observed distribution of frequencies does not belong to any law which differs in principle from Poisson's law. As a measure for evaluating the accuracy of semi-quantitative determination it seems reasonable to use the value λ – the only parameter of the Poisson distribution. Knowing the value of λ, it should always be possible to find the expected distribution of the results of a determination by using equation (2), and thus evaluate the reliability of the results obtained. The form of the Poisson distribution depends on the value of λ. When $\lambda < 1$, then the first member (the member with M = 0) will be the greatest, and will be greater the smaller λ; when $1 < \lambda < 2$, then the second member will be a maximum (m = 2) – this is illustrated in the Fig. In the examples



Graphs illustrating the occurrence of a discrete, random error conforming to Poisson's distribution.

given by us, λ varies within the limits 0.4 to 1.14. The difference in the values of λ is amenable to a clear-cut physical interpretation. Thus, the fact that during determination of copper, we obtained a value of λ = 0.40, has its basis in the high concentration sensitivity of the Cu line Cu 2824.4 A on the basis of which the determination was made. This line is convenient for visual evaluation of concentration and is not subject to self-rotation in the working concentration range. This same is true of the line W 2896.4 A, which we used for determination of tungsten; in this case we obtained a value of 0.39 for λ. On the other hand, the silver line Ag 3280.7 A, according to which this element was determined, is self-rotatory early on, and is masked by the background; accordingly, it does not possess a high concentration sensitivity. In addition, the background interferes. As can be seen from Table 2, in this case λ = 1.14.

When evaluating a method, naturally, in addition to the value of λ, it is also necessary to indicate the multiplicity of the scale of the concentration range, by means of which the determination was carried out and the limit of the sensitivity of the method, so that it is possible to take into account possible asymmetry within the

*It is necessary to point out that a Poisson distribution will only hold for a completely determined method of coding the errors, chosen so that conditions are obeyed which are essential for the discrete, random values to conform to Poisson's law. If the coding system suggested above is changed, the Poisson distribution may not be fulfilled. For example, if the series of numbers 0, 1, 2, 3. . . are used, not for coding the analytical errors, but for coding the analytical results so that the content of a test material below a certain limit is coded as zero, the first result determined by unity, the second by two etc. then, during successive repeated analyses of the same sample, we shall again obtain a series of discrete values, but in this case, the distribution will not be a Poisson distribution. Here the discrete values cannot be regarded as random events connected with some interval t, such that the possibility of the occurence of an event in the small interval Δt will be proportional to Δt.

given frequency group. If it should be necessary to compare the accuracy of methods, obtained for scales of different multiplicities, then, as indicated above, it should be possible to use the relation $\lambda = kt$. Thus, during determination of niobium (Table 3) on a two-fold scale ($t = 1/2$) we get $\lambda = 0.6$; this permits one to assume that for a three-fold scale ($t = 1/3$) we should have $\lambda = 0.4$.

In conclusion we shall consider some concrete examples of the characteristics of the method suggested in this article for evaluating experimental errors. Let us assume that a determination is carried out on a two-fold concentration scale, and that for a sample containing 0.2%, we have obtained two results 0.4 and 0.01%. From the point of view of normal evaluation of errors, we would obtain an error of 100% in both cases, and should expect the occurrence of these errors with equal probability. On the basis of the method we have suggested above, we would code the first result by the number m = 1, while the second results would be coded m = 4, and the probabilities of the occurrence of these results should be essentially different. Available experimental data indisputably confirm this last position. From the viewpoint of geologists using the results of semi-quantitative determinations, these two results are also essentially different. In the first instance the experimental result and the reliably established content of the test material in the sample are of the same order while in the second case the experimental result differs from the reliably established value by more than one order – this could lead to considerable misunderstanding when use is made of the experimental results. As a second example let us consider the following: during the determination of a component present to the extent of 0.01%, two results were obtained, 0.001 and 0.1%. The first method of calculation gives, in the first instance an error of 90%, while in the second instance the error is 900% – we are dealing with errors of different order. When calculations are made on the basis of the method suggested in this article, in both cases the deviations would be coded by the same number – the probability of the occurrence of these errors is the same – such a result would be more natural for semi-quantitative determinations.

Considerations analogous to those adduced here show that during qualitative determination, one might expect the occurence of a binomial distribution. It has been shown in [12] that the error involved during the determination of the percentage of cementite in a micro-section can be evaluated by means of a binomial distribution, if this value is evaluated by means of a large number of successive qualitative determinations, where the observer randomly touches the micro-section with a sharp point, and notes whether or not the point falls on a grain of cementite or on a part of the micro-section surface which is free from cementite. Thus we get the following scheme for the application of distribution to analytical errors: for quantitative determination – normal distribution; for semi-quantitative determination – Poisson distribution; and for qualitative determination – binomial distribution.

SUMMARY

Semi-quantitative spectrographic analysis is widely used in geological prospecting, the results usually being presented by means of a specially developed scale of discrete values. It has been shown that the distribution of the errors for the determinations is essentially different from the normal one, and can be presented with a certain degree of approximation by the Poisson distribution.

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THE USE OF RADIOACTIVE ISOTOPES FOR STUDYING THE SPATIAL DISTRIBUTION OF ELEMENTS IN THE PLASMA OF A D.C.ARC DURING THE SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN URANIUM

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In a previous communication [1] we considered some of the methods of using radioactive isotopes for studying the processes of evaporation and excitation of the elements in various sources, during spectrographic analysis. In particular, attention was given to the possibility of using them for studying the spatial distribution of elements in arc plasma. The present article is devoted to the first results of these investigations. They provide new material for coming to a decision regarding the role of the "carrier", which, according to the suggestion of Scribner and Mullin [2] is often used for increasing the sensitivity of the spectrographic determination of a number of elements.

The study of the nature of the distribution of the atoms of various elements in the space of a d.c. arc was carried out by photographing the inter-electrode gap of the source in the gamma-rays of the radioactive isotopes of the test elements. The latter were introduced into uranoso-uranic oxide in the form of oxide powders or as solutions of their nitrates, (with subsequent calcining and then grinding the base in a mortar); after evaporation together with the atoms of the appropriate impurities, they were distributed according to some law or other in the inter-electrode space of the source. The distribution of the elements in the arc plasma was registered on a photographic plate in the gamma-rays of the isotope by means of a camera-obscura. At the same time, in order to study the distribution of the excited atoms of the same elements in the arc space, the inter-electrode gap was photographed through an interference filter. Comparison of the photographs of the arc taken simultaneously in gamma- and monochromatic rays emitted by the atoms or ions of the element, made it possible to draw some conclusions regarding the changes in the intensity of their emission in various regions of the arc plasma, and the law of temperature distribution. When the photographs were taken through the light filter, the optical system was controlled by a diaphragm so that the time required for obtaining satisfactory photographs of the arc in the rays of the element and in the gamma-rays was the same.

All the chemical operations connected with preparing the standards and samples, as well as the loading of the electrodes were carried out in a protective chamber by means of manipulators. The arc with radioactive isotopes (total activity about 400-600 m. Curies) was placed in a lead camera-obscura, prepared in the form of a cabinet and provided with protective devices and manipulators, which made it possible to change the electrodes at a safe distance, and made it possible for the research worker at a window to control the arc holder. Observation of the operation of the system was made with the aid of a periscopic system. A container with electrodes which had been prepared for the tests were placed in the camera-cabinet before commencing a test.

In order to prevent the ventilation system of the laboratory from becoming contaminated with radioactive dust from the material evaporating in the arc, the air sucked from the camera was passed through a protective filter. The general appearance of the experimental setup is shown schematically in Fig. 1. The casette with the photographic film for registering the image of the arc in the gamma-rays was placed in a box outside the camera-obsura, and was only subjected to radiation from the rays passing from the outlet opening of the camera. The optimum ratios between the dimension of the outlet opening of the camera-obscura and its distance from the films were chosen experimentally: diameter of the opening about 1 mm; distance — 100 mm; value of the inter-electrode gap 4 mm. Under these conditions, when working with samples with the activity indicated above, fairly

intense and clearly-defined images of the arc were obtained, when the radiation was allowed to fall on the film for 18-20 minutes. The time for which an element is found in the arc plasma, obviously, depends on its volatility. Accordingly, the time during which readily volatile elements are found in the arc space is short, and is no longer than a few minutes; in choosing the specific activity of the radioisotopes it was essential in order to obtain sufficiently intense photographs, to photograph several samples in succession on the same place on the film. Under these conditions, in order to avoid distortion of the true picture of the distribution of the elements in the arc plasma, it was necessary to adopt special measures in order to maintain a constant distance between the electrodes in series of successive experiments. A large part of the photographs obtained in the course of the work described here for the distribution of various elements in the source plasma (Fig. 2) only gives an idea of the mean distribution of elements during the time of exposure.

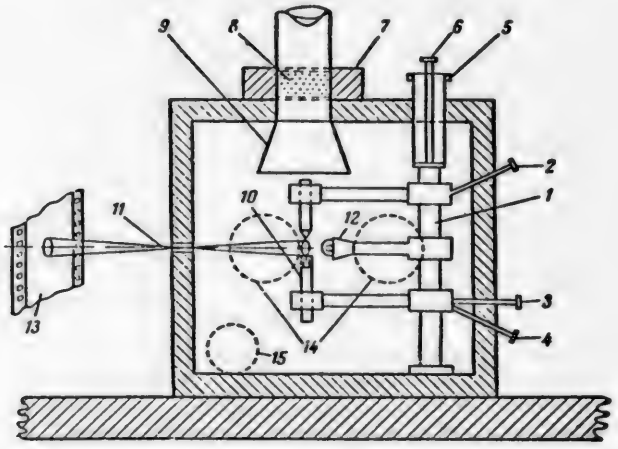

Fig. 1. Schematic features of the setup:
1) Arc holder; 2, 3, 4) handles for controlling the instruments used for adjusting the horizontal displacements of the upper and lower electrodes; 5, 6) handle for separate vertical control of the electrode displacements; 7) protective lead ring filter; 8) protective filter in the ventilation system; 9) funnel-shaped opening; 10) arc electrodes; 11) opening of the camera-obscure; 12) lamp for accurate setting of the electrodes on the optical axis by shadow projection; 13) film (casette not shown); 14) openings for manipulators and for changing the electrodes; 15) openings for loading the camera with containers containing electrodes.

For carrying out quantitative photometric measurements on the photographs, and for constructing curves showing the spatial distribution of the elements in the plasma of a D.C. arc, sensitometric curves were obtained for the photographic materials used for the gamma-rays. Blackening marks were projected on each of the films from a point source of gamma-rays by exposing various parts of the film at varying distances (r) of the photographic plates from the radiation source. Sensitometric curves were drawn within the coordinates S = f(Log r).

Curves for the spatial distribution of a large number of elements in the arc plasma were obtained. In Fig. 3, for example, are shown the most typical of them; these relate to elements possessing different volatilities (Sb, Ca, and Ta) and different ionization potentials. It is evident that the volatility of an element at the temperature established in the plasma of a D. C. arc, under the experimental conditions used, has a decisive influence on the shape of the distribution curves. On the curve for the spatial distribution of sodium (Fig. 3d) there is clearly shown the effect of the concentration of the sodium ions near the cathode in the d.c. arc; naturally this is not observed during work with an a.c. arc (Fig. 9b). The shape of the distribution curve for a given element, and the position of its characteristic points, are reproduced quite well from test to test.

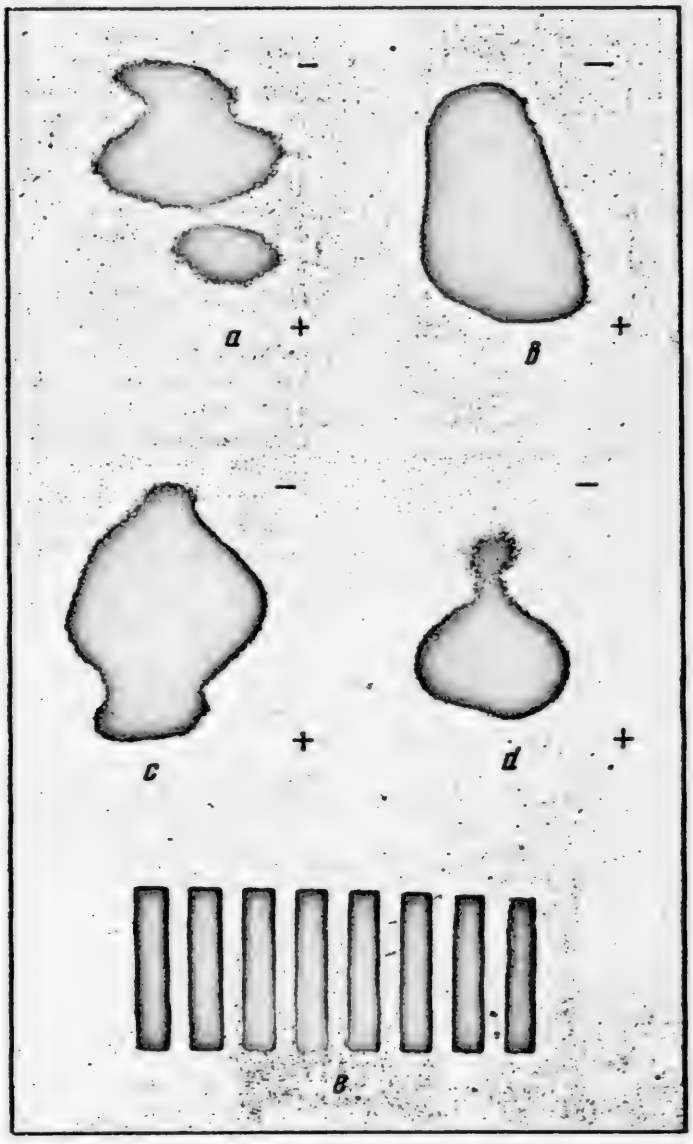

Fig. 2. Photographs taken in the gamma-rays of the radioactive isotopes Zn^{65}, Na^{24}, Ga^{72}, and Co^{60} which are characteristic of these elements in the plasma of a d.c. arc during their evaporation from uranoso-uranic oxide (I = 8 amperes); a) for sodium; b) for cobalt; c) for gallium; d) for zinc; e) blackening marks.

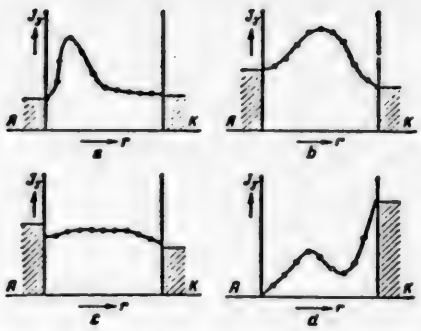

Fig. 3. Typical curves for the spatial distribution of various elements in the inter-electrode gap of a d.c. arc during evaporation of impurities from uranoso-uranic oxide: a) for antimony; b) for gallium; c) for tantalum; d) for sodium; A – anode; C – cathode.

Of considerable interest was the study of the effect of a "carrier" on the nature of the distribution of atoms of impurities during their evaporation from uranoso-uranic oxide. As is known, the mechanism governing the increase in sensitivity of spectrographic determination of impurities in the presence of a "carrier" (e.g., Ga_2O_3 or AgCl), has not yet been explained, while the hypothesis advanced by the authors of the method [2] to explain the action of a "carrier", has, apparently, not received experimental confirmation [3]. One's attention is also drawn to the contradictory results obtained by various authors who have made a study of the effectiveness of this technique for enhancing the sensitivity of spectrographic analysis during the analysis of various materials under differing conditions. The curves shown in Fig. 4 illustrate the effect of the addition of various amounts of carrier (Ga_2O_3) to test sample of uranoso-uranic oxide, on the nature of the distribution of an impurity – antimony (about 0.05%) – in the inter-electrode space of the source. As is evident from Fig. 4, while the distribution curves for antimony in the plasma differ sharply from the corresponding curves for gallium at relatively low contents of the "carrier" in the test samples, at gallium oxide contents greater than 1%, the curves for antimony completely duplicate the curve for the spatial distribution of gallium in the arc plasma.

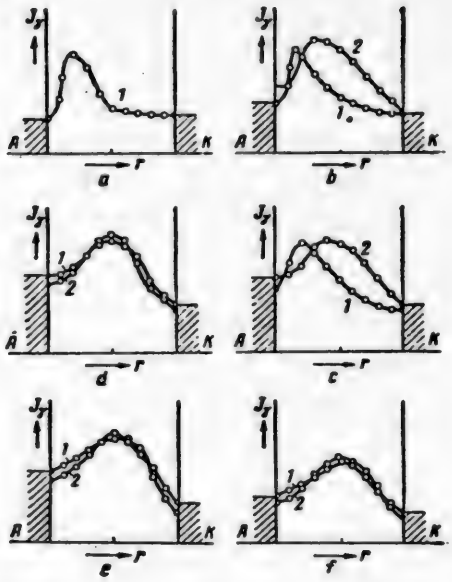

Fig. 4. Curves for the spatial distribution of antimony (1) and gallium (2) in samples with varying contents of "carrier" (gallium oxide): a) in the absence of any carrier in the sample; b) Ga_2O_3, 0.1%; c) Ga_2O_3, 0.5%; d) Ga_2O_3, 1%; e) Ga_2O_3, 2%; f) Ga_2O_3, 3%.

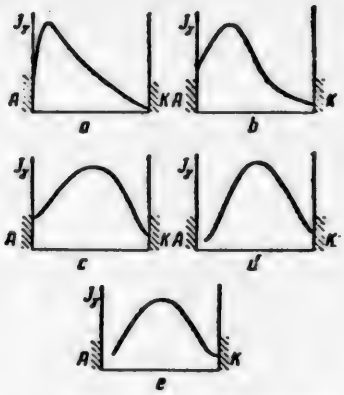

Fig. 5. Change in the spatial distribution curves for antimony with time, during its evaporation from a sample of uranoso-uranic oxide containing 2% Ga_2O_3 and 1% Sb_2O_3: a) 10 seconds after the arc has started to burn; b) 15 seconds after; c) 20 seconds after; d) 25 seconds after; e) 30 seconds after.

The curves in Fig. 5 illustrate the development of this process with time, the example taken in the case being one which contains 2% of gallium oxide and 1% antimony oxide.

As is evident from Fig. 5, in the course of the first 20 seconds (Curves a, b) there is observed a gradual transition from an asymmetric spatial distribution curve, which is characteristic of antimony atoms free from gallium,

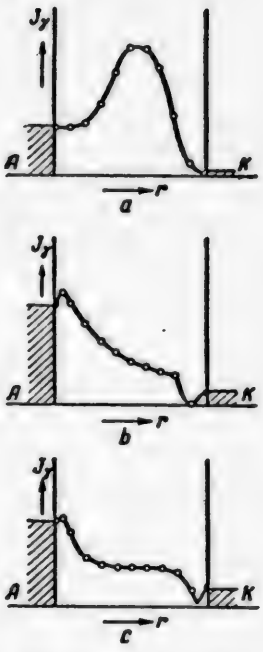

Fig. 6. Curves for the spatial distribution of silver during its evaporation from uranoso--uranic oxide; the silver was present as AgCl (a), Ag_2O (b), and metal (c).

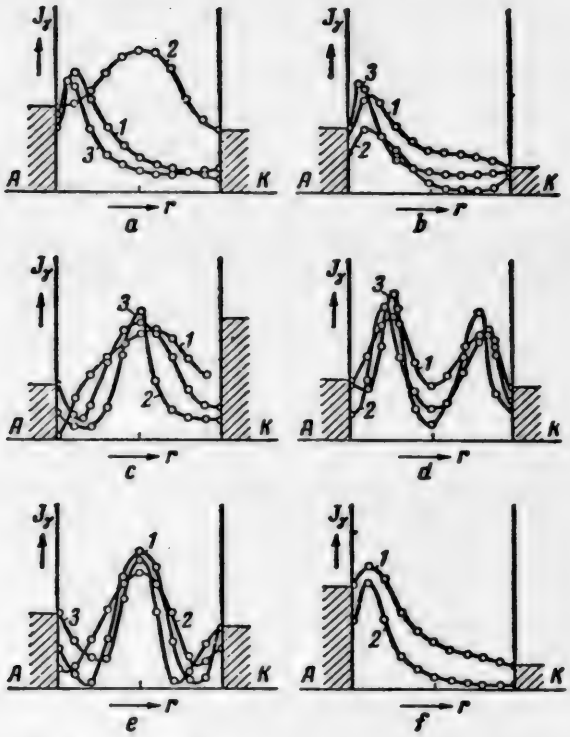

Fig. 7. Spatial distribution of antimony (1), gallium (2), and copper (3) when present together in uranoso--uranic oxide in various proportions: a) curves for antimony, gallium, and copper during the evaporation of each of them taken separately; b) Sb_2O_3 0.1%; CuO 1%; Ga_2O_3 0.1%; c) Sb_2O_3 0.1%; CuO 1%; Ga_2O_3 2%; d) Sb_2O_3 0.1%; Ga_2O_3 2%; CuO 2%; e) Sb_2O_3 0.1%; Ga_2O_3 30%; CuO 10%; f) Sb_2O_3 10%; Ga_2O_3 2%.

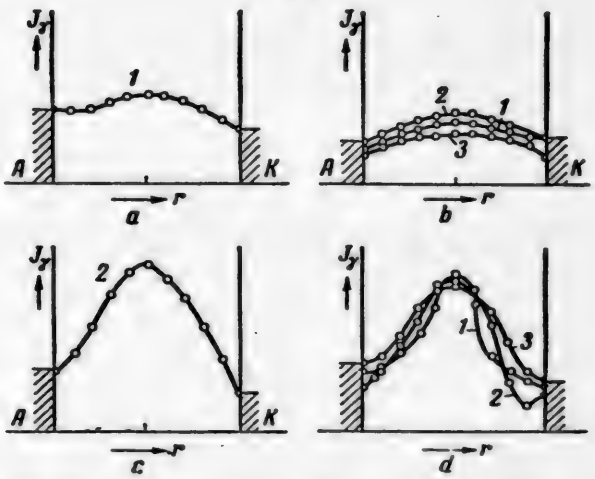

Fig. 8. Effect of calcium and gallium on the distribution curves of sodium in a d.c. arc. Curves (a) and (c) for calcium and gallium alone. Curves 1, 2, and 3 (b) and (d) relate to calcium, gallium, and sodium respectively.

to a symmetrical "gallium" distribution, to which the antimony atoms conform during the expiration of this time (curves c, and d).

It can be shown experimentally that the displacement of the maximum for the distribution of antimony to the middle of the inter-electrode gap proceeds in parallel to an increase in the content of the atoms of gallium passing into the arc plasma.

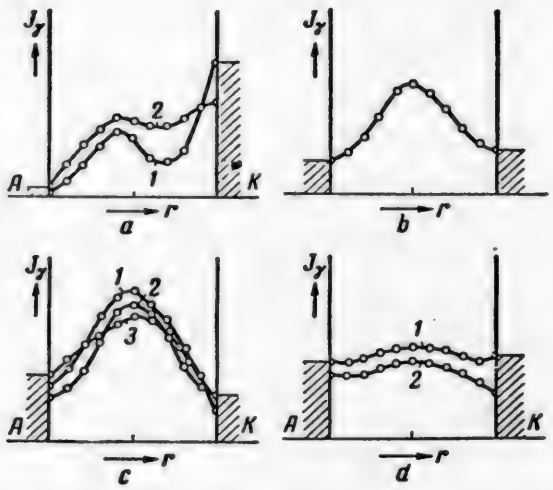

Fig. 9. Spatial distribution of sodium, calcium, and gallium during their evaporation from uranoso--uranic oxide containing varying amounts of these elements: a) fro sodium (1) using gamma-rays, in the absence of the other two impurities, and using a d.c. arc. Curve (2) was obtained using the line 5688 Al; b) for sodium, using gamma-rays in an A. C. arc; c) for gallium (1) and sodium (2) when present in the sample in amounts of 2% and 0.01% repsectively. Curve (3) for sodium was obtained using the line 5688 A; d) for calcium and sodium when these elements were present in the sample in amounts of 10% and 0.01% respectively.

The presence of "carrier" atoms in the arc plasma, thanks to the dome-like curve for the spatial distribution of the atoms which is characteristic for the "carrier", and which has a sharp maximum along the middle of the inter-electrode gap, leads, in this way, to a forced concentration of impurity atoms in the central region of the plasma. To this should be related the decrease in the extent of scattering of the atoms of the impurity elements, and their transfer from the discharge, and consequently, the increase in intensity of their characteristic spectral lines. It was shown experimentally that the nature of the distribution of "carrier" atoms in the arc space and the redistribution of impurity atoms in the plasma connected with this, do not depend on the method of introducing the "carrier" in the inter-electrode gaps of the source. The simultaneous presence of "carrier" and impurity atoms in the test sample is not necessary for ensuring the redistribution mentioned above of impurity atoms in the arc space under the influence of carrier atoms. Evaporation of impurity and "carrier" (taken in an appropriate ratio to the impurity) into the plasma can be carried out separately also.

Examination of the results given in Fig. 6 leads one to think that the mechanism indicated above to explain the effect of gallium oxide on the nature of the distribution of impurity atoms in the plasma, and on the intensity of the lines of these elements, in the spectrum, could be completely, or at least partially, extended to cover the effect of other "carriers" which are used in spectrographic analysis; e.g., a carrier like AgCl. The same results show that the curves for the distribution of silver atoms in the inter-electrode gap, and the possibility of the occurrence of this "carrier" effect, all other conditions being equal, depend on the type of compound used and the manner in which this element is introduced into the test sample. It might be thought that the state in which the silver atoms appear in the arc plasma during their evaporation from uranoso-uranic oxide, in which they were present as the chloride and in the two other cases which were considered, is not the same. This question is being treated in greater detail at the present moment. We shall only note that, as our tests have shown, the shape of the curves for decreasing activity of the test base containing AgCl with labelled Ag^{110} or Cl^{36}, depending on the time of arc burning*, proved to be absolutely identical.

Interesting, and from our point of view, important results for the understanding of the role of the "carrier" and some other phenomena observed during spectrographic analysis, were obtained in the course of a study of the spatial distribution of impurities during their evaporation from uranoso-uranic oxide, containing, in addition to "carrier" , large amounts of other elements, e.g., calcium and copper, whose atoms are distributed in the arc

*For the method of obtaining these curves, see [1, 4].

space according to another law which is different from that governing distribution of gallium. Some of the results relating to these experiments are shown graphically in Figs. 7-9; they convincingly demonstrate the arbitrary nature of the concept of "carriers" , and the close connection between the results of the "carrier" effect on the spatial distribution of atoms of the impurity in the plasma of a d.c. arc, and the presence and relative content of other elements in the test sample. In the presence of two macro-components, the atoms of which are distributed differently in the arc space, the impurities will follow the atoms of the component that is present in the greater amount in the test sample. A particularly good example of the effect of macro-components on the nature of the distribution of impurities, and of elements contained in the test sample in smaller amounts than the main components, are the curves relating to sodium (Figs. 9 a, c, d).

Comparison of the distribution curves for gallium permits one to observe a certain characteristic which is common to them, namely the relation between the width of the concentration zone of the elements in the space of a d.c. arc and the relative content of the elements in the test sample.*

Taking into account all that has been said above, the following basic conclusions can be drawn:

1. The spatial distribution of atoms of different species in the plasma of a d.c. arc (presumably, just as in other sources) is not the same. The nature of this distribution depends, in the first instance, on the volatility of the element (or that of its compounds) at the temperature established in the source under the experimental conditions used. In the case of elements with low ionization potentials, under favorable conditions, there occurs a concentration of the ions of the element in the region near the cathode, when a d.c. arc is used. The shape of the spatial distribtuion curve for an element is almost independent of its content in the test sample.

2. If the difficultly volatile base contains in addition to the test impurity, a large amount of another element (we shall call this the macro-element), the atoms of which are distributed in the inter-electrode space according to a law which differs from that governing the distribution of the impurity, then, starting at a certain content, the macro-component will dictate the distribution of the atoms of all the other elements in the source space. In the presence of two macro-components – the atoms of which are distributed differently in the arc space – the impurity-elements (without any regard for the law governing the spatial distribution of their own atoms in the source) will follow the atoms of the macro-component present in the greater amount in the test sample. When the relative amounts of the macro-components are similar to each other, the impurities will be attracted by each of them in equal measure.

3. The elements which are the components of compounds normally used in spectrographic analysis as "carriers", and which favor an increase in the sensitivity of such an analysis, are characterized by a symmetrical, dome-like, distribution of the atoms in the space of the arc, with a sharp maximum at the center. The nature of the distribution of the "carrier" atoms in the arc space is independent of the method adopted for introducing it into the inter-electrode gap. The increase in intensity of the analytical lines of the impurity elements which is sometimes observed under favorable conditions when a "carrier" is used, is in no way connected with changes in the rate at which these elements pass into the plasma; this rate, as we have shown experimentally, and as results already published have shown [3], remains unchanged. The "carrier" only affects the distribution of the impurities in the inter-electrode space of the source, and leads to their compulsory concentration in the central region of the plasma. A consequence of this is a decrease in the degree of scattering and the passage of the atoms of the impurities out of the discharge. Accordingly, the effect of the "carrier" on the intensity of the spectral lines is not selective in character. In certain cases, for example when the sample contains large amounts of elements whose atoms are distributed in the arc plasma more asymmetrically than the atoms of the "carrier", the effect of the "carrier" may be weakened considerably or liquidated completely.

4. Differences in the spatial distribution of the elements in the inter-electrode gap, and the effect on this distribution of the composition of the test materials, may be one of the important factors which determine the relationship between the results of spectrographic analysis and the bulk composition of the samples, and the presence in these samples of so-called "ternary components".

This factor, however, has not hitherto been taken into account sufficiently and should be specially and systematically studied in the future.

*It should be pointed out that all the processes described occur before uranium vapors pass into the plasma. Accordingly, the distribution of uranium atoms in the arc has no effect on the distribution of the other elements considered.

SUMMARY

Radioactive tracers have been used experimentally for the first time for studying the longitudinal distribution of elements in the plasma of a d.c. arc. Active isotope distribution in the plasma was recorded in gamma-rays by means of a camera-obscura made of lead. The spatial distribution of atoms of various elements in the plasma of a d.c. arc has been shown to be different, and to depend on the volatility of the elements.

The reasons for the effect of the carrier on the sensitivity of spectrographic determination of impurities in uranium have been ascertained. A symmetrical dome-like distribution of the atoms in the arc space, with a sharp maximum in the center is characteristic of the carrier, irrespective of the method by which the carrier is introduced into the arc gap.

The carrier only affects the distribution of the elements in the inter-electrode gap of the source, and leads to a compulsory concentration of the impurities in the central region of the plasma in accordance with the distribution of the carrier.

The effect of the carrier is not selective in character. It may be considerably reduced when large amounts of elements with a spatial distribution differing from that of the carrier are present in the sample.

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EXTRACTION-PHOTOMETRIC DETERMINATION OF TANTALUM, BORON, INDIUM, AND RHENIUM

N. S. Poluetkov, L. I. Kononenko, and R. S. Lauer

Extraction-photometric methods are those methods in which an element is determined on the basis of the color of its compounds in an organic solvent after extraction of an aqueous test solution to which the requisite reagent has been added.

Recently, methods have been suggested for the determination of a number of metals (Table 1) which were based on the photometric measurement of colored extracts containing the metal to be determined in the form of the salt of a complex halogen acid with a basic dye, the complex being of the form $A_n \cdot Me \cdot X_m$, where A is the organic dye; Me is the test metal; and X is the halogen.

TABLE 1

Determination of Elements by Photometric Measurements of an Extract Containing a Compound of a Halogen Acid and a Dye

Element	Halogen acid	Dye	Solvent
Gallium	$HGaCl_4$	Rhodamine C	Benzene [1]
Gold	$HAuCl_4$	Rhodamine C	Isopropyl ether [2]
Antimony	$HSbCl_6$	Rhodamine C	Benzene [3-4]
"	$HSbCl_6$	Methyl Violet	Benzene [5]
Thallium	$HTlCl_4$	Rhodamine C	Benzene [6]
"	$HTlCl_4$	Methyl Violet	Benzene [7]

The same dye is a reagent for a number of metals (Table 1) while the requisite selectivity is achieved by the choice of halogen, acidity of the solution, and other experimental conditions. In order to discover new extraction-photometric methods, it is important to take into account the parallelism which exists between the extractability of simple or complex halogen acids according to an oxonium mechanism [8] and in the form of salts with organic bases. All the complex chloro acids of the metals mentioned in Table 1, and which are extracted in the form of salts with organic dyes, are extracted by diethyl ether or some other oxygen-containing solvents. On the other hand, simple or complex acids of the elements extracted by an oxonium mechanism are also extracted by solvents not containing oxygen in the form of arsonium compounds (Table 2).

It may be assumed, therefore, that in the case of elements whose acids are extracted according to an oxonium mechanism, or in the form of salts of arsonium compounds, conditions may be selected so that these acids can be extracted in the form of salts with basic dyes. This permits one to determine along what lines search should be made for new extraction-photometric methods. It should be borne in mind, however, that acids which are only weakly extracted according to an oxonium mechanism may not be extracted with dyes. Thus, As^{III}, Sb^{III}, Ge^{IV}, Te^{IV}, and other materials, which are only weakly extracted by diethyl ether from hydrochloric acid solutions [14], are not extracted in the form of rhodamine salts under analogous conditions. This is connected, presumably, with the fact that the concentration of the rhodamine base is several times less than the concentration established by the main component – the solvent – during extraction according to an oxonium mechanism.

The correctness of the concepts outlined above can be illustrated taking as examples new methods for determining tantalum, boron, indium, and rhenium which are described below.

TABLE 2

Extractability of Certain Elements in the Form of Complex or Simple Acids According to an Oxonium Mechanism and in the Form of Arsonium Salts

Element	Anion extracted	Solvent for extraction according to an oxonium mechanism	Extraction in the form of arsonium salts	
			Arsonium compound	Solvent
Fe	$Fe(SCN)_6^{3-}$	Diethyl ether	Triphenylmethylarsonium	o-Dichlorobenzene [9]
Co	$Co(SCN)_4^{2-}$	Diethyl ether and amyl alcohol	Triphenylmethylarsonium	o-Dichlorobenzene [10]
Co	$Co(SCN)_4^{2-}$	"	Tetraphenylarsonium	Chloroform [11]
Re	ReO_4^-	Ketones [12]	Tetraphenylarsonium	Chloroform [13]

1. Determination of Tantalum

According to an oxonium mechanism, tantalum can be extracted in the form of a complex fluoro acid by means of ketones, with its simultaneous separation from titanium and niobium [15, 16]. We found that from solutions containing hydrofluoric acid, tantalum can also be extracted in the form of salts with organic dyes of the diphenyl- and triphenylmethane series, and diazine, triazine, and phthalein dyes (auramine, fuchsine, methyl violet, base bright green, rhodamine, etc.) the solvents used for extraction being benzene, diethyl ether, etc. Accordingly, it is possible to determine tantalum on the basis of the color of the extract, which may be yellow, red, green, etc., depending on the dye chosen. The reaction is characterized by high specificity – the reaction is not given by niobium and titanium, nor by a number of other metals; calcium and the rare-earths, however, depress the intensity of the color given by tantalum.

Using methyl violet as the dye, and benzene as solvent, it was found that the optimum value of the pH of the solution is 2.3; the concentrations of the dye and the hydrofluoric acid in the solution being extracted should be strictly defined. Extraction with benzene should be carried out immediately after addition of methyl violet; the benzene extracts should not be kept in contact for a long time with glass (before photometric determinations are carried out, the extracts may be kept in platinum or porcelain crucibles). Of the other elements, only boron gives a color similar to that of tantalum; nevertheless, boron can be removed by evaporation with hydrofluoric and sulfuric acids. Colored extracts are also given by the nitrate and iodide ions, as well as divalent mercury.

Under the conditions described below, about 80% of the tantalum present is removed after one extraction; this, however, does not reflect on the accuracy of its determination, when it is borne in mind that the percentage extraction of tantalum is the same during preparation of both the standards and the test solutions.

Determination of Tantalum in Ores. 0.1-4, 0-6.0% Ta_2O_5. 50 mg of the finely ground ore is treated in a platinum crucible by heating with 5 ml of hydrofluoric acid to which 5-6 drops of concentrated sulfuric acid has been added. The solution is evaporated to dryness on a sand bath, and the residue fused with 2 g of sodium pyrosulfate on a gas burner and heated until liberation of SO_3 ceases, without overheating the residue. The salt in the crucible is then extracted with 25 ml of 4% ammonium oxalate, and the solution transferred to a 100 ml beaker; the crucible walls are carefully washed with distilled water, taking care, however, that the volume in the beaker does not exceed 35-40 ml. The solution is heated to the boil, and then cooled to room temperature; it is finally transferred to a 50 ml standard flask and diluted to the mark with water. In order to remove suspended particles of calcium oxalate 10-20 ml of the solution is centrifuged for 10 minutes. Filtration instead of centrifuging is not suitable in this case because high results are obtained, presumably, as a result of leaching out of nitrate ions from the filter, and these ions give the same reaction as tantalum. 4 or 2 ml of the centrifugate is taken for the determination. If less than 4 ml is taken, the volume of the solution is made up to the requisite value by addition of blank solution. The colored benzene extract is obtained by adding 2 ml of water, 2 ml of hydrofluoric acid (1.5 N), 5 ml of benzene, and 2 ml of 0.1% aqueous methyl violet, to 4 ml of test solution contained in a separating funnel. After extraction, and after the layers have been allowed to separate, the benzene extract is centrifuged in a dry

centrifuge tube for 20-30 seconds, and the optical density measured in an FEK-M photoelectric colorimeter, using a 3 mm cell, and a yellow filter; the reference solution is benzene. The filter is a combination of a green light filter, provided with the apparatus, and an orange glass, and has a maximum transmission at about 580 mμ. A calibration curve is constructed for 10, 25, 50, and 75 γ of Ta (Fig. 1). A standard stock solution is first prepared containing 250 γ Ta/ml, by dissolving 25 mg of the metal or the corresponding amount of tantalum pentoxide in 3-5 ml of hydrofluoric acid to which has been added nitric acid (2 drops of the concentrated acid). The solution is evaporated to dryness and the residue fused with 4 g of sodium pyrosulfate until sulfuric acid ceases to be evolved. The melt obtained is leached with 50 ml of 4% ammonium oxalate solution, this extract is boiled and then cooled, and finally diluted to the mark in a standard 100 ml flask. From this stock solution a working solution with a concentration of 50 γ Ta/ml is prepared by diluting 10 ml of the former to 50 ml with black solution. The latter is prepared by fusing 4 g of sodium pyrosulfate and dissolving the melt obtained in 50 ml of a 4% solution of ammonium oxalate; this solution is then diluted to 100 ml with water. When constructing the calibration curve, the standard solution of Ta is made up to 4 ml with this blank solution; extraction is then carried out as described above.

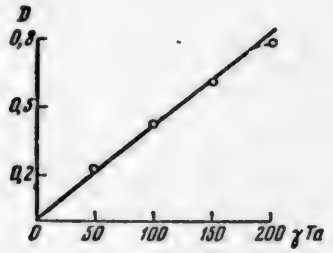

Fig. 1. Calibration curve for the determination of tantalum by means of methyl violet.

TABLE 3

Reproducibility of Replicate Determinations of Tantalum in Ores

Ta_2O_5 determined, in %		Mean	Deviation from the mean, in %
First determination	Second determination		
0.62	0.58	0.60	3.3
0.85	0.92	0.885	3.9
0.91	0.93	0.92	1.1
3.36	3.29	3.325	1.1
3.11	3.11	3.11	0
4.33	4.45	4.39	1.4
4.88	4.82	4.85	0.6
5.37	5.43	5.4	0.6
6.1	6.1	6.1	0

Table 3 illustrates the reproducibility of replicate determinations of tantalum in ores.

2. Determination of Boron

Boron can be extracted as the methyl-violet salt of hydrofluoric acid, just as in the case of the fluoro complex with tetraphenylarsonium. The latter was used for the preliminary separation of boron [17]. We chose the conditions for determination of small amounts of boron on the basis of this principle.

1-2 ml of the neutral test solution is placed in a platinum crucible and mixed with 0.5 ml of 2 N hydrofluoric acid and 0.1-0.2 ml of 20% sodium acetate solution; water is then added to bring the volume up to 3 ml, and the solution heated to the boil in order to get complete formation of fluoroborate. The solution is cooled and transferred to a quartz test tube; 3 ml of benzene is added followed by 0.5 ml of 0.2% methyl violet solution, and the whole shaken. The benzene layer, which is colored violet when boron is present, is poured into a centrifuge tube in which it is centrifuged for several minutes; the optical density of the centrifugate is measured on a FEK-M photocolorimeter using a 3 mm cell and a yellow filter. The relation between the value of the optical density and the amount of boron is linear up to 20 γ of boron (Fig. 2).

In Fig. 3 is shown the relationship between the intensity of the color obtained for 20 γ of boron and the amount of 0.2% methyl violet solution added.

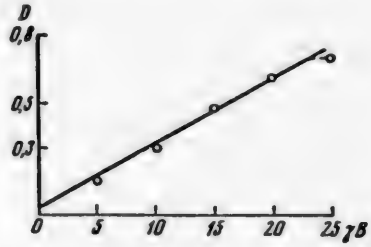

Fig. 2. Calibration curve for determination of boron by means of methyl violet.

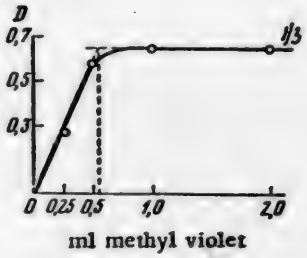

Fig. 3. Relation between the color intensity of the benzene layer and the amount of methyl violet solution added, when the amount of boron taken is 20 γ.

As the curve shows, the color becomes a constant at about 0.55 ml of methyl violet solution or 1.1 mg of the solid material. Thus, 20 γ of boron or $\frac{20 \cdot 10^{-6}}{10.8} = 1.85 \cdot 10^{-6}$ g-atom of boron corresponds to $\frac{1100 \cdot 10^{-6}}{556} = 1.97 \cdot 10^{-6}$ g.mole of dye (assuming that methyl violet is, mainly, the hydrochloride of pentamethylrosaniline $C_{24}H_{28}N_3Cl \cdot 9H_2O$). From this it fillows that 1 atom of boron corresponds to $\frac{1.97}{1.85} = 1.07$ molecules of methyl violet, so that the colored compound of boron has the formula (methyl violet) BF_4.

TABLE 4

Control Determination of Boron in Boric Acid Solution

Boron taken, in γ	Boron found, in γ	Difference, in γ
3.0	3.4	+0.4
8.0	8.4	+0.4
12.0	11.6	−0.4
14.0	14.0	0
18.0	17.2	−0.8

About 90% of the boron present is extracted during one extraction when the optimum conditions chosen are used, and the pH is 3.4 while the amount of boron taken is 20 γ. This incomplete extraction of boron does not, however, affect the accuracy of determination, as is evident from the following table – Table 4.

As for the selectivity of the reaction, what was said above of the reactions for tantalum is also true for boron.

3. Determination of Indium

Indium is extracted with diethyl ether from a medium of 3-5 N HBr as its ether compound with $HInBr_4$ [18]; in the same way, the compound of indium with a dye, for example, the bromoindiate of rhodamine C, is extracted with benzene.

The indium compound can be extracted from a medium of 1.3-4.2 N HBr with benzene; nevertheless, with increasing acidity, the color of the benzene layer becomes less intense. The color of a blank solution is stronger for lower values of the hydrogen bromide concentration; the optimum value for the intensity is obtained at a hydrogen bromide concentration of 2.5-2.8 N. As established experimentally in the course of experiments with radioactive indium, during extraction of 5 ml of an aqueous solution containing 0.5 ml of 0.5% aqueous rhodamine C solution by means of 5 ml of benzene, 28, 43, 34, and 24% of the indium present (50 γ) passed into the extract, when the HBr concentration was 1, 2, 3, and 4 N respectively.

The amount of indium extracted can, however, be increased to 95%, by adding acetone (1 ml) during the extraction; when this technique is used the color of the blank solution also increases. The optimum conditions were found to be: HBr concentration 2.5 N, amount of rhodamine C 1 ml of 0.25% solution, acetone 0.5 ml, volume of aqueous solution 10 ml and volume of benzene 25 ml; under these conditions, the optical density (from 0 to 1.1) at 530 mμ is directly proportional to the indium concentration – up to 50 γ of indium (the cell used was 5 mm and the photometer a Pulfrich photometer).

The reproducibility of the results obtained for determination of indium according to this method is shown in Table 5.

TABLE 5

Determination of Indium in Indium Chloride Solutions

In taken, in γ	In found, in γ	Difference, in γ	In taken, in γ	In found, in γ	Difference, in γ
6.3	6.0	−0.3	35.0	35.5	+0.5
7.5	8.0	+0.5	42.5	43.0	+0.5
18.8	18.5	−0.3	50.0	50.0	0
22.5	23.0	+0.5	72.5	72.0	−0.5

Of the other methods, a similar reaction is given by trivalent gold, molybdenum, tungsten, trivalent thallium, and iron, quadrivalent tellurium, and selenium, and divalent manganese. Divalent iron as well as Ca, Ga, Cr^{III}, Ti, Th, Bi, Be, Pb, As^{III}, U^{IV}, V^{V}, Ni, Co, Zr do not interfere. Trivalent iron can be reduced with ascorbic acid. 5 γ of indium can be determined in the presence of 10 mg Fe^{II} after addition of about 0.05 g of ascorbic acid to the solution prior to extraction.

During determination of indium in complex mixtures, it should be removed beforehand from the presence of interfering elements.

4. Determination of Rhenium

As mentioned already, rhenium, in the form of rhenic acid or its anion ReO_4^-, can be extracted both from acid and from alkaline solution by ketones [12]; this can be explained by the capacity of perrhenates to form oxonium compounds with ketones. Tests have shown that rhenium can be extracted with methylene blue using ethyl acetate as the extractant; with methyl violet, using ethyl acetate as extractant, when extraction is carried out from ammoniacal and neutral media, and chloroform for extracting from a sulfuric medium; with auramine from sulfuric acid media, using chloroform and ethyl acetate as extractants; with rhodamine, using the same solvents from neutral solution, and ether from sulfuric acid media.

For quantitative determination of indium, extraction of the perrhenate of methyl violet with ethyl acetate from a neutral solution can be used. When the volumes of the aqueous and ethyl acetate phases are 5 ml, and the amount of methyl violet is 1 ml of a 0.1% aqueous solution, from 1 to 100 γ of Re can be determined by using a Pulfrich photometer and a 5 mm cell in conjunction with a filter which has maximum transmission at 610 mμ. The optical density is linearly related to the rhenium concentration (up to 100 γ Re). Although a number of anions interfere (such as nitrate, iodide, and bromide), the reaction has the advantage that it can be used for the determination of rhenium in the presence of molybdenum. The latter can be masked readily with tartrate; by carrying out the reaction in the presence of 0.2 ml of 40% Seignette salt, it is possible to determine 1 to 100 γ of rhenium in the presence of 20-70 mg of molybdenum trioxide.

TABLE 6

Control Determinations of Rhenium in a Mixture Containing 40 mg Molybdenum Trioxide

Re taken, in γ	Re found, in γ	Difference, in γ	Re taken, in γ	Re found, in γ	Difference, in γ
5.0	5.0	0	22.5	22.0	−0.5
12.5	12.8	+0.3	25.0	24.8	−0.2
15.0	14.4	−0.6	30.0	30.0	0
17.5	17.5	0	32.5	32.0	−0.5

Table 6 contains the results for control determinations of rhenium in the presence of 40 mg MoO_3, taken in the form of ammonium molybdate.

SUMMARY

Simple or complex acids of elements, which are readily extracted according to an oxonium mechanism, or in the form of salts with organic high-molecular weight bases, such as the arsonium compounds, can also, in many instances, be extracted in the form of their salts with basic dyes. On the basis of this fact, new extraction-photometric methods have been developed for the determination of tantalum, boron, indium, and rhenium.

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OXIDATION REACTIONS IN INTERNAL ELECTROLYSIS AND THEIR USE IN CHEMICAL ANALYSIS

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All the variants of the method of internal electrolysis proposed hitherto have been based on the deposition of the reduced element on an indifferent electrode [1-13]. Nevertheless, during internal electrolysis, it is possible to deposit the test element in an oxidized state on the indifferent electrode; for this purpose, the electrode which can be reduced (e.g. PbO_2), is connected with an indifferent electrode (e.g., a platinum electrode), and the electrode system formed immersed in a solution containing the test ion which is capable of being reduced. In this way thallium has been determined by deposition as Tl_2O_3 [14]. Ions of other metals, which are deposited on the anode during ordinary electrolysis [15] can also be determined by the method of internal electrolysis when a correct choice has been made of the oxidizing agent in the sleeve (catholyte). In the present article the possibility of such determinations is demonstrated. In the work described here the same setup as that used for the determination of thallium was used; the only difference was that a carbon electrode, provided with a means of attaching a platinum electrode to it, was immersed in the catholyte. The external appearance of the apparatus is shown in Fig. 1.

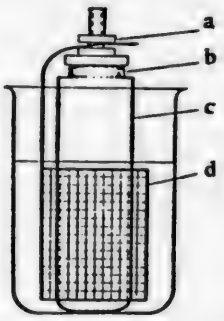

Fig. 1. Apparatus for carrying out internal electrolysis using an oxidation process on an indifferent electrode: a) screw; b) carbon electrode; c) sleeve containing oxidizing agent; d) platinum electrode.

Deposition of Manganese Dioxide* on the Anode

In order to establish the oxidation reaction: $Mn^{2+} + 2H_2O - 2e = MnO_2 + 4H^+$, it is essential to connect the sleeve of PbO_2 with the platinum electrode and immerse the whole in a solution of a divalent manganese salt. The galvanic element thus obtained $PbO_2 \| PbSO_4 / / Mn^{2+} \| MnO_2(Pt)$ with short circuited electrodes will operate in the direction of the formation of manganese dioxide, since the normal oxidation potential of the pair: $PbO_2 + 4H^+ + SO_4^{2-} / PbSO_4 + 2H_2O$ ($E_h^0 = +1.685$ volt) is considerably higher than the oxidation potential of $MnO_2 + 4H^+ / Mn^{2+} + 2H_2O$, which is equal to 1.28 volt.

The oxide of manganese $MnO_2 \cdot nH_2O$ which is deposited on the anode from a solution of $MnSO_4$ contains various amounts of water; the composition of the deposit depends to a very large extent on the rate of electrolysis. The higher the electrolysis rate, the higher the water content of the precipitate. During rapid deposition of manganese, the ratio $MnO_2 : H_2O$ in the deposit always differs on the platinum electrode. Nevertheless, when deposition of manganese is carried out slowly it is possible to get reproducible results; in this case, the composition of the precipitate which is deposited on the anode corresponds to the formula $MnO_2 \cdot H_2O$; the deposit answers the requirements of a gravimetric form.

*Experiments on the anodic deposition of manganese were carried out in conjunction with B. Iordanov.

The composition of the precipitate obtained during anodic oxidation of Mn^{2+} may vary between $MnO_2 \cdot H_2O(H_2MnO_3)$ and $MnO_2 \cdot 2H_2O(Mn(OH)_4$ or H_4MnO_4. When the pH of the anolyte is constant, the composition of the deposit should correspond to the formula $MnO_2 \cdot 2H_2O$, when the electrolysis is carried out with a high rate, and $MnO_2 \cdot H_2O$ when the rate approximates zero.

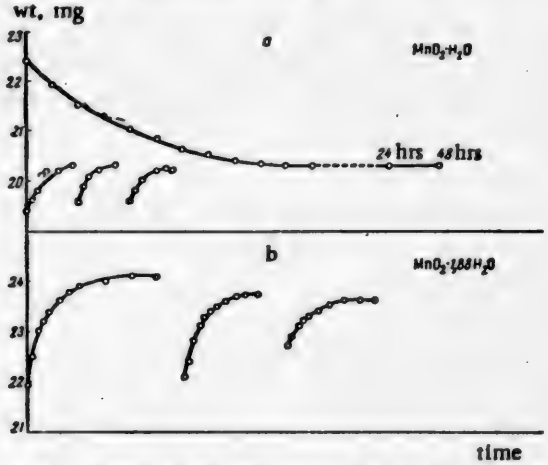

Fig. 2. Changes in the precipitate of $MnO_2 \cdot H_2O$ which does not have a stoichiometric composition, during drying.

Slow electrolysis can be achieved by observing the following conditions simultaneously: 1) the sleeve should be coated with a thick film of collodion; 2) the catholyte should be prepared from a mixture of PbO_2 and Na_2SO_4 in the ratio 20 : 1 (parts by weight) and moistened with 2 N H_2SO_4. The results obtained for determination of manganese in this way are considerably better than those obtained when a cathode is used (up to a certain limit, of course); this fact is probably a consequence of the sulfatization of PbO_2, as a result of which the total rate of electrolysis is decreased; 3) the pH of the anolyte should be kept at about 4.5.

The precipitate of $MnO_2 \cdot H_2O$ which is deposited on the anode is of a dark-brown color, and adheres quite firmly to the platinum, while the light-brown deposit whose composition corresponds to $MnO_2 \cdot 2H_2O$ (obtained during rapid hydrolysis) separates readily from the electrode.

The deposit formed during slow deposition, after washing in succession with distilled water, ethyl alcohol, and ether, weighs more than would be expected on theoretical grounds. Nevertheless, the weight of the precipitate decreases in air, and after approximately one hour its composition corresponds to the formula $MnO_2 \cdot H_2O$. The same phenomenon is observed when the deposit is left in a desiccator containing $CaCl_2$ for 20-30 minutes. After drying in the desiccator the weight of the deposit is always lower than would correspond to $MnO_2 \cdot H_2O$, but on standing in air the deposit absorbs water and acquires the expected weight. Loss and gain of water is a reversible process (Fig. 2a).

Manganese is determined as follows. A sleeve with a wall 2 mm thick is covered with a thick collodion film by immersing it 5-6 times in a 10% collodion solution. After immersion, the sleeve is left in the air for about 5 minutes, while after the last immersion it is left in the air for 15 minutes. The sleeve is preserved by filling it with a saturated solution of Na_2SO_4. When a sleeve filled with a mixture of PbO_2 and Na_2SO_4 in the ratio 20 : 1 is used, it is moistened with 2 N H_2SO_4; a thick carbon electrode is immersed in it, this electrode being provided with a nut and screw for fixing the platinum grid to it. The solution containing Mn^{2+} is poured into a 100 ml beaker and diluted to 30 ml with water; 3 ml of a saturated solution of CH_3COONH_4 is added followed by 0.5 g of NH_4NO_3 in order to increase the conductivity of the anolyte. Under these conditions a solution with a pH of about 4.5 is obtained; the pH remains almost constant during the whole duration of the electrolysis. The solution is then heated to 80° and the electrodes immersed in it. Heating is stopped and a slow stream of air passed through the anolyte. Electrolysis takes about 3 hours when about 15 mg of manganese is to be determined, while it takes about 5 hours for the determination of about 25 mg Mn. When electrolysis is complete, the platinum electrode is washed with water, ethanol, and ether; it is then placed in a desiccator containing $CaCl_2$ for 30 minutes, and then left in the air until the weight is constant.

The Table contains results obtained for the determination of manganese as $MnO_2 \cdot nH_2O$. The concentration of the $MnSO_4$ solution was established by precipitating the manganese as $MnNH_4PO_6$, and weighing as $Mn_2P_2O_7$. Electrolysis was carried out until a negative reaction was given for Mn^{2+} with $(NH_4)_2S_2O_8$.

TABLE

Mn taken in g	$MnO_2 \times \times H_2O$ calc., in g	$MnO_2 \times \times nH_2O$ found, in g	Mn calculated, in g	Relative error, in %	Duration of electrolysis, in hours
0,0078	0,0149	0,0149	0,0078	± 0,0	2,0
0,0078	0,0149	0,0149	0,0078	± 0,0	2,0
0,0087	0,0166	0,0167	0,0087	± 0,0	2,5
0,0106	0,0203	0,0276	0,0145	+36,8	0,5
0,0106	0,0203	0,0237	0,0124	+17,0	1,0
0,0106	0,0203	0,0201	0,0105	— 0,9	2,0
0,0106	0,0203	0,0203	0,0106	± 0,0	2,0
0,0106	0,0203	0,0205	0,0107	± 0,9	3,0
0,0157	0,0300	0,0300	0,0157	± 0,0	3,0
0,0157	0,0300	0,0301	0,0158	+ 0,6	3,0
0,0174	0,0332	0,0330	0,0173	— 0,6	3,5
0,0174	0,0332	0,0333	0,0174	± 0,0	3,5
0,0174	0,0332	0,0332	0,0174	± 0,0	4,0
0,0217	0,0415	0,0413	0,0216	— 0,5	5,5
0,0266	0,0508	0,0504	0,0264	— 0,7	5,0
0,0266	0,0508	0,0505	0,0264	— 0,7	5,5
0,0269	0,0513	0,0594	0,0311	+15,6	2,0

The tabulated data show that satisfactory results can be obtained for manganese by slow precipitation, when $MnO_2 \cdot H_2O$ is deposited on the electrode (correction factor 0.5234). The mean relative error is ± 0.7%. During rapid electrolysis, i.e., when a sleeve with only a thin covering of collodion is used and the pH of the anolyte is kept at >4.5, the results obtained for manganese are not satisfactory. Qualitative detection of Mn^{2+} can be carried out under similar conditions.

Precipitation of mangenese dioxide on a platinum electrode is speeded up considerably by heating the solution to 60-70° and adding NH_4NO_3; the latter increases the conductivity of the electrolyte. Deposition of precipitate depends to a very large extent on the hydrogen ion concentration of the anolyte. The sensitivity of the reaction decreases considerably at pH's less than 4.0.

Mn^{2+} is identified as follows. The test solution is neutralized by means of dilute Na_2CO_3 solution to a weak acid reaction (in the presence of γ-dinitrophenol as indicator) and then heated to 60-70°. NH_4NO_3 is added to the solution and the setup for internal electrolysis with a catholyte of PbO_2 + dilute H_2SO_4 immersed in it. When Mn^{2+} is present a brown precipitate of $MnO_2 \cdot nH_2O$ will appear on the anode. When no deposit appears in the course of 15 minutes, it can be concluded that the solution does not contain Mn^{2+}. Using this technique, Mn^{2+} can be detected at a concentration of $0.8 \cdot 10^{-5}$ g Mn/ml in the presence of Ag^+, Al^{3+}, As^{5+}, Ba^{2+}, Be^{2+}, Bi^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cs^+, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, Li^+, Mg^{2+}, Na^+, NH_4^+, Ni^{2+}, Pb^{2+}, Rb^+, Sr^{2+}, Tl^{3+}, Ti^{4+}, UO_2^{2+}, Zn^{2+}, Zr^{4+}, MoO_4^{2-}, NO_3^-, SO_4^{2-}, VO_3^- and WO_4^{2-}. Small amounts of Cl^- ions do not interfere either.

Deposition of Lead Dioxide on the Anode

If a small excess of potassium or sodium hydroxide is added to a solution containing Pb^{2+}, and electrodes for carrying out internal electrolysis with a catholyte of $K_2S_2O_8 + H_2O$ (E_h^0 of the process: $S_2O_8^{2-} + 2e = 2SO_4^{2-}$ amounts to +2.05 volt) immersed in this solution of Pb^{2+}, then the reaction $PbO_2^{2-} - 2e = PbO_2$ will occur on the anode; as a result of this reaction a precipitate of lead dioxide will be formed on the platinum electrode. Sulfate ions which may penetrate into the anolyte do not interfere with deposition of lead dioxide, since the anolyte contains excess alkali in which $PbSO_4$ readily dissolves.

The brown deposit of lead dioxide may be formed not only by using the catholyte $K_2S_2O_8 + H_2O$, but also by using $NaBiO_3 + HNO_3$ ($E_h^0 > +1.8$ volt) etc. The deposit formed on the anode is very dense and adheres firmly to it.

At present, work is being carried out with the aim of improving the conditions for the quantitative determination of lead. These experiments show that the most suitable oxidizing agent for deposition of lead dioxide is $K_2S_2O_8$.

Deposition of the Hydroxide of Trivalent Nickel on the Anode

$K_2S_2O_8 + H_2O$ is placed in the sleeve. A precipitate of nickel trihydroxide is deposited on a platinum electrode from an ammoniacal solution of divalent nickel, because the oxidation potential of the pair $S_2O_8^{2-} + 2e = 2SO_4^{2-}$ is higher than the oxidation potential of the pair $Ni_2O_3 \cdot xH_2O + 6H^+ / 2Ni^{2+} + (x + 3)\,H_2O$ ($E_h^0 = +1.75$ volt). Under these conditions the following process occurs on the anode: $2Ni^{2+} + (x + 3)\,H_2O - 2e = Ni_2O_3 \cdot xH_2O + 6H^+$ since simple nickel ions form the complex ions $[Ni(NH_3)_6]^{2+}$. Simultaneously with deposition of nickel hydroxide on the anode, nickel hydroxide is also formed in solution, as a result of which the solution becomes turbid, and the bottom and the walls of the vessel in which electrolysis is carried out are covered with a film of deposit.

Similar experiments with a solution of a cobalt salt showed that the hydroxide of trivalent cobalt only deposits from solution at high Co^{2+} concentrations, and then only in insignificant amounts.

Deposition of Halogen Ions on the Anode

From tables of oxidation potentials [16] it is evident that the normal oxidation potentials of the system: $I_2 / 2I^-$ ($E_h^0 = +0.5345$ volt), $Br_2 / 2Br^-$ ($E_h^0 = +1.0652$ volt) and $Cl_2 / 2Cl^-$ ($E_h^0 = +1.3583$ volt) are lower than the value of the potential of the pair: $PbO_2 + 4H^+ + SO_4^{2-}$ $PbSO_4 + 2H_2O$ ($E_h^0 = +1.685$ volt). Consequently, on immersion in a solution containing I^-, Br^- or Cl^- of a sleeve covered with a film of collodion and containing a catholyte consisting of PbO_2 + dilute H_2SO_4, the sleeve being connected to a platinum electrode, the following respective processes, will occur: $2I^- - 2e = I_2$, $2Br^- - 2e = Br_2$ and $2Cl^- - 2e = Cl_2$.

The capacity of I^-, Br^-, and Cl^- to be oxidized on an anode when the internal electrolysis method is used, can be applied for analytical purposes.

Since the potential of the oxidation reactions of I^-, Br^-, and Cl^- will differ appreciably from one another, one might expect that during continuous electrolysis, iodide ions will be oxidized first, they will be followed by the bromide ions, while the chloride ions come last. The iodine, bromine, and chlorine thereby liberated in succession can be readily detected by appropriate reactions.

During internal electrolysis such reactions as: $I_2 + 2H_2O - 2e = 2IO^- + 4H^+$ and $2\,IO^- + 4\,H_2O - 8e = 2IO + 8H^+$ * may also occur. Furthermore, at high concentrations of Cl^- or Br^- and a low concentration of I^-, after oxidation of the latter, oxidation of Br^- and Cl^- starts immediately, which can also lead to incorrect results, since conditions are created such that I_2 can be oxidized to IO^- and even to IO_3^-: $I_2 + Cl_2 + 2H_2O = 2IO^- + 2IO^- + 2Cl^- + 4H^+$ and $I_2 + 5Cl_2 + 6H_2O = 2IO_3^- + 10Cl^- + 12H^+$. Nevertheless, all these difficulties which occur during detection of I^- at low concentrations in the presence of Br^- and Cl^- can be avoided, if the electrolysis process is interrupted from time to time.

When the solution contains I^-, then the blue color formed with starch during electrolysis does not permit one to distinguish the yellow color arising from bromine. But, if sufficient KCl is added to the solution, and, after detection of I^-, the electrolysis is carried out continuously, then the Cl_2 liberated will oxidize I_2 to IO^- or to IO_3^-, as a consequence of which the blue color of the solution disappears.

Detection of iodine and bromine ions in mixtures of I^-, Br^-, and Cl^- is carried out by observing the following conditions: 2 ml of solution is poured into a small beaker and 1-2 drops of starch solution added, followed by about 0.5 g of solid KCl. A sleeve containing PbO_2 + dilute H_2SO_4 and in contact with a platinum wire wound in a spiral around the sleeve is immersed in the solution. If the solution remains colorless, then the sleeve is immersed once again for a short time. When the solution contains I^-, then in order to detect Br^- it is necessary to carry out the electrolysis continuously until the solution is colorless, after which the yellow color given by bromine with starch appears.

The method permits determination of I^- at a limiting concentration of 1 : 100,000 and at ratios of I : Br equal to 1 : 10,000 and of I : Cl equal to 1 : 30,000 for amounts of $5.0 \cdot 10^{-5}$ g. Bromine ions can be detected

* E_h^0 of the pair $2IO_3^- + 12H^+ / I_2 + 6H_2O$ amounts to 1.195 volt.

at a limiting concentration of 1 : 40,000 and at a ratio of Br : Cl equal to 1 : 30,000, the amount being $5.0 \cdot 10^{-4}$ Small amounts of I^- and Br^- are detected almost immediately.

Separate Oxidation of I^-, Br^-, and Cl^-

When internal electrolysis of a solution containing I^-, Br^-, and Cl^- at the same time, is carried out using a galvanic element containing, for example, a ferric salt in the cathode compartment (E_h^0 of the pair: Fe^{3+}/Fe^{2+} = = +0.771 volt) or Hg + H^+ (E_h^0 of the pair: $HgO + 2H^+/Hg + H_2O$ = +0.926 volt) or Hg^{2+} (E_h^0 of the pair: Hg^{2+}/Hg = +0.854 volt) etc., then even when electrolysis is carried out continuously only oxidation of I^- will occur.

In the presence of KBr + KCl (and starch), and using a mixture of HgO + water in the cathode compartment, only oxidation of iodine ions occurs. The presence of bromide or chloride ions, not only does not interfere with the oxidation of I^- to I_2, but actually favors this oxidation, since the conductivity of the electrolyte increases considerably, and a blue color appears almost immediately.

Using a setup which consists of the galvanic element: $MnO_2 \| Mn^{2+}/2Br^- \| Br_2$ (Pt), it is possible, by continuous electrolysis of the solution, to oxidize Br^- without oxidizing the bromine liberated to BrO^- or BrO_3^-. The possibility of carrying out such an oxidation becomes understandable when one bears in mind that the potentials of the pair: $Cl_2/2Cl^-$, $HBrO + H^+/Br^- + H_2O$ and $BrO_3^- + 6H^+/Br^- + 3H_2O$, are respectively equal to: +1.3583 volt, + 1.35 volt, and + 1.44 volt.

Thus, during electrolysis of a solution containing I^-, Br^-, and Cl^- using a mixture of HgO and water in the cathode compartment, it is possible to oxidize I^- alone. A setup with a catholyte consisting of MnO_2 + dilute H_2SO_4 permits oxidation of I^- and Br^- but not Cl^-. Finally, using a mixture of PbO_2 + dilute H_2SO_4, it is possible to oxidize I^- as well as Br^- and Cl^-.

Using the galvanic element $HgO/Hg/2I^-/I_2$(Pt), iodide ions are readily detected in solutions containing down to $3.3 \cdot 10^{-5}$ g/ml iodine.

A very characteristic feature of oxidative internal electrolysis is the fact that by choosing the appropriate catholyte (oxidizing agent) it is possible to prepare a galvanic element – a setup for internal electrolysis – by means of which it is possible to carry out precisely the anode reaction required and to prevent the remaining oxidation processes. In this connection, oxidative internal electrolysis can be regarded as a method of electrolytic oxidation with control of the anode potential.

SUMMARY

It has been shown that by using the method of internal electrolysis it is possible to deposit on an anode made of an indifferent material, not only Tl_2O_3, but also the oxides of quadrivalent manganese and lead, trivalent nickel, and also to oxidize halide ions.

It has been established that it is possible to determine manganese quantitatively by precipitating it on the anode as $MnO_2 \cdot H_2O$. The average error is ± 0.7%. Methods are described for the identification of Mn^{2+}, and for detection of iodine and bromine ions in mixtures of I^-, Br^-, and Cl^-. Taking as an example the separate oxidation of I^-, Br^-, and Cl^-, it has been shown that oxidative internal electrolysis can be regarded as a method of electrolytic oxidation in which the anode potential is controlled.

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THE USE OF ULTRA-SOUND IN ANALYTICAL CHEMISTRY

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During recent years ultra-sound has been attracting the attention of research workers in the most diverse fields. In particular, ultra-acoustic methods are finding wide application in the practice of physico-chemical research; they are rapidly penetrating into the normal practice of physico-chemical scientific-research and production laboratories. Ultrasonic vibrations can cause oxidation and reduction, depolymerization, various molecular arrangements, "aging" of precipitates, depolymerization during electrolytic processes etc. Ultra-sound helps the study of the properties of materials and the laws governing various processes [1-7]. The setups necessary for generating ultra-sound have been described in the literature and are available to any laboratory.

The aim of the present article is to draw the attention of analytical chemists to the use of ultra-sonic methods, for solving theoretical and practical problems in analytical chemistry.

Of the greatest importance, in our opinion, for analytical chemistry, are the following properties of ultra-sound:

1. The relation between the velocity of sound in solutions and mixtures and the concentration of dissolved material, and the possibility arising from this of carrying out quantitative determination of compounds and individual elements.

2. The depolarizing effect of ultra-sound and the acceleration of the electrolytic deposition of the elements.

3. The effect of vibration (sounding) of gases under the action of an intermittent stream of thermal radiation, and the optical-acoustic method of analyzing gases and the method of studying absorption spectra in the infra-red based on this.

4. The dispersing, coagulating, agitating action of ultra-sound; oxidation in an ultra-sonic field; the change in the rate of dissolution of materials, etc.

Of near-analytical importance is the application of ultra-sound for the determination of ion solvation; the use of the values of adiabatic compressibility, calculated from acoustic measurements, as "properties" in physico-chemical analysis, and the possibility of the identification of organic compounds.

The Relation Between the Velocity of Sound in Solutions and the Concentration of Dissolved Material [8-16]

It has been established that the rate of ultra-sonic vibrations in solution depends on the concentration of dissolved material, and, in certain cases, particularly for solutions of electrolytes, this relation is linear or almost linear. In Figs. 1 and 2 are shown curves relating the velocity of ultra-sound to the concentration of certain salts of uni- and divalent metals, and curves for aqueous solutions of some sugars. The relationship indicated above (linearity or near-linearity) is obeyed in both cases, as can readily be seen.

On the basis of assumptions regarding the additivity of internal energy in solution, Kudriavtsev [14] derived a formula relating the velocity of sound in the solution to the concentration of dissolved material, and to the velocity of sound in the pure solvent:

$$c^2 = (1 - \nu)\, c_0^2 + \nu \cdot 2{,}32 \cdot 10^7 \cdot \Phi_0,$$

where γ is the percentage by weight of the dissolved material in solution; c_0 is the velocity of sound in the solvent; Φ_0 is the energy of the ionic crystalline lattice of the dissolved material. The values for the velocity of ultra-sound in aqueous solutions of a number of halides and nitrates of the alkali metals, as calculated by this formula, are in good agreement with the experimental values.

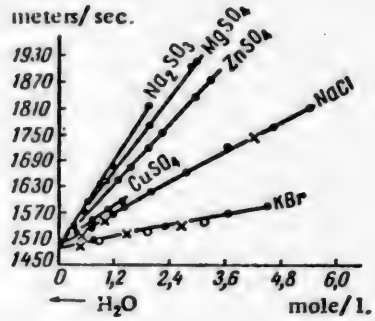

Fig. 1. Curves relating the velocity of ultra-sound and concentration of dissolved material for a number of salt solutions. Experimental values: o) P. Porozov; X) A. Posynskii; o) E. Freier [9-11].

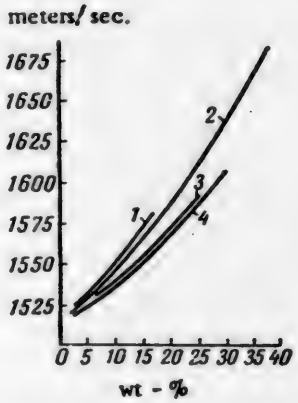

Fig. 2. Curves relating the velocity of ultra-sound and concentration of the dissolved material for aqueous solutions of some sugars: 1) D-fructose; 2) D-glucose; 3) raffinose; 4) saccharose [15].

As for mixtures of liquids: in the case of dissociating liquids, the velocity of ultra-sound is again linearly dependent upon the concentration, whereas in the case of non-dissociating liquids the relationship is often more complicated [16].

The existence of such a relationship means that it should be possible to carry out a quantitative determination of chemical compounds on the basis of measurements of the velocity of ultra-sound in solution; Sokolov [17] was the first to draw attention to this possibility. In order to carry out such a determination, Babikov [18, 19] used an impulse method for measuring the velocity of ultra-sound, and made an apparatus which enabled very small changes in this velocity to be measured. The basic components of an ultra-sonic impulse setup are: a generator of electric vibrations, a piezo-electric converter, a tube receiver, and an oscilloscope. Ultra-sonic impulses are generated by the quartz plate of the converter from electrical impulses, and, after passing through the test medium, are converted back again into electrical impulses. In Babikov's apparatus (USIS - apparatus for measuring the velocity of ultra-sound) ultra-sonic impulses following each other in a definite sequence are passed through the solution. These impulses are of very low intensity so as to exclude the possibility of the interaction of ultra-sound with the medium. When the concentration of the solution changes, there is a corresponding change in the velocity of ultra-sound, and there is a displacement of the impulses on the screen of the oscilloscope; the value of this displacement gives an indication of the change in concentration. Using a calibration curve constructed beforehand, it is easy to determine the amount of material in solution. The method possesses high accuracy and measurements can be carried out in a moving flow without taking samples. In this way the concentration of aqueous solutions of NaCl, the concentration of alcohol in water, and also the amount of methanol in ethanol have been determined. The error in the determination of alcohol is 0.1%.

Other methods such as the method of standing waves, the method of light diffraction in an ultra-sonic field, etc. [1, 20-22] can be used for the accurate measurement of the velocity of ultra-sound, as well as the impulse method. In all cases, however, the intensity of the ultra-sonic vibrations should be low enough to avoid their interaction with the medium.

We are speaking, really, therefore of a new method of physicochemical analysis. It is very desirable that there should be further studies in evaluating both the general possibilities and limitations of the method, and further studies on its practical use.

The Effect of Ultra-Sound on Electrolysis

Ultra-sonic vibrations of sufficiently high intensity lead to cavitation in a liquid medium – cavitation is a break up of the continuous medium, the spaces being filled with the vapors of the liquid and gases dissolved in the liquid. During the transition from rarefaction zones to compression zones, the cavitation bubbles begin to "swing" and during this process there occur local changes in pressure, temperature jumps, and electric discharges. Calculations show that the pressure may increase to several thousand atmospheres, while the temperature may rise to 2500° and higher. These phenomena lead to the activation of the oxygen and nitrogen dissolved in the water, while hydrogen peroxide, nitrous and nitric acids are formed. In addition to this cavitation effect, ultra-sonic vibrations at the same time lead to intensive agitation. This, presumably, accounts for the dispersion, coagulation, diffusion, crystallization, and dissolution which thereby occur.*

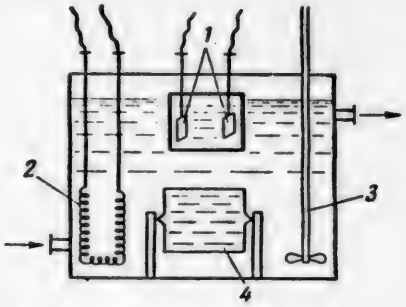

Fig. 3. Setup for studying electro-deposition by means of ultra-sound: 1) electrodes; 2) temperature regulator; 3) stirrer; 4) ultra--sound emitter.

The effect of ultra-sonic vibrations on electro-chemical processes is very diverse [23]; it is expressed primarily in the depolarizing effect and in a decrease in deposition potential. Furthermore, "sounding" during electrolysis can lead to changes in the composition and character of electrolytic deposits, and can alter the duration of deposition, and the current yield etc.

By using ultra-sound, the hydrogen over-voltage on the cathode can be decreased to such an extent that it becomes possible to deposit aluminum and magnesium from aqueous solutions [24]. Irradiation with ultra-sound leads to a drop in the deposition potential of nickel, copper, and silver [25], and considerably cuts down the time required for the electro-deposition of copper [26] and lead [27]. For example, quantitative deposition of 0.3 g of lead takes only 20 minutes instead of one hour usually necessary for ordinary electrolysis. Work carried out by Kochergin and Terpilovsskii [28] on the effect of an ultra-sonic field on the electro-crystallization of metals, taking Cu, Ni, Co, Pb, and Sn as examples, has allowed several important conclusions to be drawn. It has been established that ultra-sonic treatment evens out the concentration of the ions at the electrodes to a considerable extent, decreases the value of the depolarization, degases the whole volume of the electrolyte, and favors the removal of bubbles of gas from the electrode surfaces, thereby permitting preparation of brighter and more dense deposits. The setup used is shown in Fig. 3. It has been shown in other papers [5] that the hardness of copper deposits obtained in an ultra-sonic field is 40% higher than that of deposits obtained under normal conditions. When the high-frequency vibrations are excited in the cathode mass itself, the metals deposited on such a cathode are of enhanced stability and possess better structures [29].

The effect of ultra-sound on the micro-structure of an electrolytic deposit may be twofold. On the one hand, the agitation effect and depolarization favor formation of deposits with crystals of large size, while the mechanical vibrations in themselves increase the number of centers of crystallization, and lead to the formation of fine-crystalline deposits [7].

Ultra-sound may prove useful during mass electrolytic determinations.

The Optico-Acoustic Effect and its Use

At the end of the last century it was established that gases and vapors which absorb the infrared, resonate on being subjected to the action of these rays, interrupted at the frequency of sound. During absorption of the radiation, the gas heats up and this leads to pressure changes. To the extent that the beam of infrared rays is interrupted the pressure becomes pulsating, i.e., sound develops. Veingerov studied this property in order to develop an optico--acoustic method of gas analysis, and to develop a method of studying the absorption spectra of materials in the infrared [30-36].

* The cavitation effect and the agitation effect can be considered in isolation; the agitation effect is itself connected with the formation of cavities. In some cases it is difficult to establish the decisive factor.

Elementary mono- and diatomic gases, O_2, N_2, and H_2, and the inert gases do not absorb the infrared; accordingly when air free from carbon dioxide and water-vapor is irradiated with the infrared no sound develops. When, therefore, a mixture of air and gaseous compound or compounds which vaporize, e.g., CO_2, is subjected to the action of an interrupted flow of radiation, the strength of the sound which develops will be proportional to the concentration of the absorbing impurity. The intensity of the sonic vibrations can be registered, for example, by means of a microphone and a galvanometer.

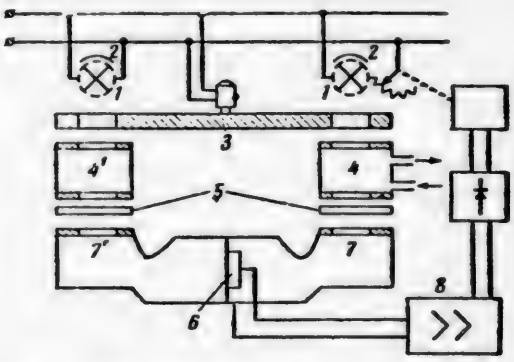

Fig. 4. Schematic diagram of M. L. Veingerov's gas-analyzer.

There are several types of gas-analyzers based on the optico-acoustic effect. The scheme of one of them is shown in Fig. 4 [37]. The infrared source is the emitter 1 provided with reflectors 2. The stream of radiation is interrupted by means of a rotating disc with opening 3. The test gas mixture passes continuously through the operating cell 4 into the reference cell 4' located in the second optical channel; this reference cell also contains a gaseous mixture with a known (e.g. zero) content of the test gas. After passing through the operating cell and filters 5, which only transmit a certain band of radiation, both sound beams pass into the cells of the differential ray-receiver 7 and 7'. Between these cells a microphone 6 is placed. When a change in concentration of the gas mixture occurs in the operating cell 4, there is a corresponding change in pressure in the ray-receiver 7; accordingly, the membrane of the microphone which experiences a difference in pressure from the sides of cells 7 and 7' will be set in vibratory motion. The alternating current which thereupon develops is registered by the galvanometer. Having calibrated the apparatus by means of mixtures with known contents of the test component, and having constructed the appropriate calibration curve, it is easy to determine an unknown concentration of the test component in a mixture.

In some cases it is possible to determine components in ternary mixtures. The method is applicable to the determination of gases which do not possess overlapping bands in their infrared absorption spectra, and also in those cases where acoustic measurements can be combined with chemical determinations of one of the components. In such cases it is advisable to use nomograms similar to those shown in Fig. 5 for the ternary mixture $He-O_2-N_2$.

Veingerov [36] has also shown the possibility of using optico-acoustic effect for studying the absorption spectra of gases and vapors in the infrared. If a known amount of gas or vapor which absorbs infrared rays is subjected to the action of a monochromatic beam of these rays, then the intensity of sound vibrations which thereupon develops will depend on the percentage absorption of the radiation of the given wave-length. By changing the wavelengths successively and registering the intensity of the sound vibrations continuously, it is possible to obtain the absorption spectrum of the material in the infrared.

The Use of the Oxidizing, Coagulating, and Other Properties of Ultra-Sound

Intensive ultra-sonic vibrations are widely used as a means of dispersing, coagulating, degassing, and mixing materials etc. Many of these effects are of considerable importance for analytical chemistry. Setups of different types, such as those described by Kuznetsov-Fetisov and Perpilovskii [38] can be used in practical work.

During a not very prolonged treatment with ultra-sound, many finely dispersed systems coagulate and can be

readily filtered; for example, such treatment accelerates the sedimentation of barium sulfate [39]. In some instances it is possible to accelerate the clearing of various solutions by means of ultra-sonics. Thus, during precipitation of zinc with ammonium sulfide in an acid medium, about 24 hours are necessary for clarification of the solution. When, however, precipitation is carried out in a vessel subjected for 30 minutes to the action of ultra-sound, complete clarification is achieved within the hour [40].

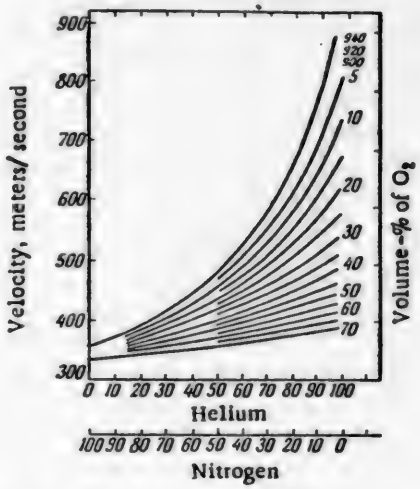

Fig. 5. Nomogram for the determination of the helium content in a mixture of $He-O_2-N_2$ saturated with water vapor
Volume-%, O_2

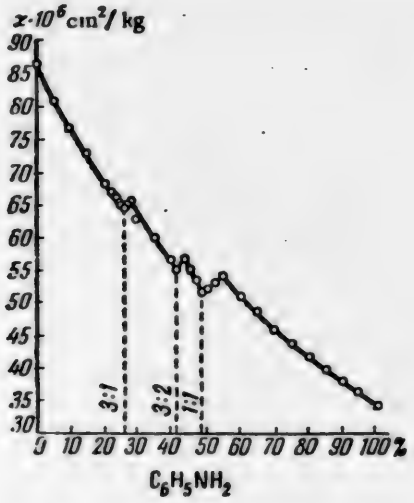

Fig. 6. Compressiblity isotherm (20°) of the system ethyl acetate — aniline.

There is little doubt that ultra-sound will find wide application in extraction processes, particularly during work with radioactive solutions, and in those cases when the use of continuous extraction is, for some reason, not expedient. It has been shown that extraction is particularly strongly accelerated when the ultra-sonic vibrations are directed at an angle to the direction of the movement of the extractant. Acceleration of extraction separation under the influence of ultra-sound is, presumably, related to a number of factors. Of importance in this connection is the increase in the area of the phase boundary as a result of emulsion formation, and the vibrations of the bubbles of extractant; the acceleration of diffusion in both liquids and the change of state of the boundary layer are also important factors [7].

Intense ultra-sonic vibrations modify the oxidation conditions in solutions [41-46]. It can be regarded as established that the oxidizing action of ultra-sound, just like the oxidation-reduction action of radioactive radiation, is secondary in origin; it is connected, as we have noted already, with the formation and subsequent "agitation" of the bubbles subjected to cavitation; changes in pressure, temperature and electrical phenomena are consequent upon this. The hydrogen peroxide, nitric acid and other oxidizing agents which are formed as the result of the activation of the hydrogen and nitrogen dissolved in the water also lead to oxidizing effects in an ultra-sonic field. Many examples of the oxidizing action of ultra-sound are known. During treatment with ultra-sound, sulfur is liberated from H_2S, while free iodine is liberated from potassium iodide solutions, and $FeSO_4$ is oxidized to $Fe_2(SO_4)_3$ etc.

The sensitivity and resolving power of photographic plates are known to be of great importance for spectrographic analysis. In this connection, therefore, the effect of ultra-sound on photographic emulsions is of interest. During treatment with ultra-sound, dispersion of silver bromide occurs. The decrease in particle size and the increase in homogeneity of the composition and concentration of silver bromide throughout the emulsion, permit one to prepare films with considerably greater sensitivity and resolving power [5, 47].

It should also be noted that ultra-sound has also been used for accelerating dissolution and for increasing the rate of heterogeneous reactions. Taking potassium ferrocyanide as an example, it has been shown that the rate at which this compound dissolves increases under the influence of ultra-sonic vibrations (even when compared with intensive mechanical agitation) [40]. Ultra-sonic radiation eliminates the chemical passivity of iron [48, 49], and

chromium [48] with respect to acids: iron dissolves in concentrated sulfuric acid, while chromium dissolves in hydrochloric acid. The number of such examples could be extended considerably (see, for examples, [50-53]).

Ultra-Sonic Methods for the Physico-Chemical Study of Materials Which Are Important in Analytical Chemistry

Determination of the degree of hydration of ions in solution is of great importance in analytical chemistry. At present, among other methods, ultra-sonic methods are also used. [54-61]. Evaluation of the degree of hydration by means of ultra-sound may be carried out by two different methods [61], the most important of which is that suggested for the first time by Pasynskii [54]. The principle of this method may be briefly stated as follows. The electric field of an ion leads, in the surrounding layers of water, to some additional pressure which decreases the compressibility of the water. Since, at a small distance from the ion this pressure may have a considerable value, it is considered that the hydrated envelope of the ion is not subjected to compression. This signifies that the velocity of sound in this envelope is infinitely large. On the basis of results on the compressibility of solutions obtained from acoustic measurements, and under conditions where the compressibility of the hydrated envelope is assumed to be zero, it is possible to calculate the value of the hydration of the ions. Adiabatic compressibility is calculated by means of Laplace's equation:

$$c = \sqrt{\frac{1}{\beta_\phi \cdot \rho}},$$

where c is the velocity of sound, β_ϕ is the adiabatic compressibility; σ is the density. Calculation of the hydration h, expressed in grams of water per gram of dissolved material, for a solution 100 g of which contains g gram of dissolved material, is carried out on the basis of the formula:

$$h = \frac{\left(1 - \frac{\beta}{\beta_0}\right)(100 - g)}{g},$$

where β and β_0 are the compressibility coefficients of the solution and solvent (water) respectively.

Of some interest is the use of the value of adiabatic compressibility as a "property" in physico-chemical analysis. During a study of the compressibility – composition curve, sharp minima have been detected, the origin of which is ascribed to the formation of chemical compounds. Such an assumption has been confirmed experimentally by studying a number of systems; for example, the system ethyl acetate–analine. It has been known for some time that compounds possessing the molar composition 3 : 1, 3 : 2, and 1 : 1 exist in this system. It was found that the compressibility of these systems exhibit sharp minima at the molar compositions corresponding to the compounds indicated (Fig. 6) [62]. It has also been demonstrated that the value of the velocity of ultra-sound can be used directly, as a property for studying ternary mixtures [63]. It has been demonstrated, however, that the development of compounds in binary mixtures is not necessarily related to anomalous changes in the velocity of sound, and, on the other hand, the existence of the velocity of sound – composition curve of minima or maxima cannot always be related to the formation of a chemical compound [64].

It should also be pointed out that it is possible to identify organic compounds on the basis of the value of the molecular velocity of sound which exhibits additivity similar to that shown by molecular refraction, the parachor, or the Van-der-Waal's constant. The value of the molecular velocity of sound is calculated according to Rao's law:

$$R = c^{\frac{1}{3}} \frac{M}{\rho},$$

where M is the molecular weight; ρ is the density; c is the velocity of sound; and R is the molecular velocity of sound which is independent of temperature. It is also possible to determine the molecular weight of dissolved materials on the basis of the value of the molecular velocity of sound [2].

SUMMARY

Ultra-sound has already been used for solving many theoretical and practical problems in analytical chemistry. The further application of ultra-sound to chemical analysis may lead to a number of interesting results of practical importance.

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A STUDY OF THE FORMATION OF THE MIXED FERROCYANIDES OF COPPER AND THE ALKALI METALS BY A POTENTIOMETRIC METHOD

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The ferrocyanides of many metals are sparingly soluble, as the result of which they are being successfully used in a number of cases in analytical chemistry. The use of potassium ferrocyanide as a titrant during the visual and potentiometric determination of zinc, lead, indium, and other metals is widely known [1]. The potentiometric method, however, would seem to have more possibilities for the determination of various metals when the soluble ferrocyanides of the alkali metals are used as titrants, since there is then no need to select indicators for fixing the equivalence point. Potentiometric titration with potassium ferrocyanide is used nowadays with varying degrees of success for the determination of zinc, cadmium, cerium, lanthanum, gallium, indium, nickel, cobalt, and other metals. Despite all the advantages of the potentiometric method, it does possess the drawback that the position of the equivalence point often depends on the nature of the alkali metal entering into the composition of soluble ferrocyanide used as titrant, and also depends on the concentration of the ferrocyanide in solution. A knowledge of the details of the mechanism of formation of the insoluble mixed ferrocyanide opens up new possibilities for the analytical use of the ferrocyanides. In particular, it is essential to make a more careful study of the relationship between the composition of the mixed ferrocyanides and the presence in solution of one or other of the alkali metals, and the concentration of the latter. Treadwell and Hall [2] have already noted the shift in the equivalence point during the potentiometric titration of certain divalent metals salts by means of $K_4[Fe(CN)_6]$ in the absence and in the presence of cesium in solution. Subsequently, similar phenomena have been observed by other authors in other cases. Considerably more information regarding this point has been obtained by the solubility method. Nevertheless, as experiment shows, far from all the mixed ferrocyanides whose formation is fixed by the results of solubility, find reflection on the potentiometric titration curves taken in the same systems.

The present article is devoted to the potentiometric titration of copper ions by $[Fe(CN)_6]^{4-}$ ions. Despite a number of published articles on this question, no reliable potentiometric method of determining copper by means of a ferrocyanide has been put forward. Of the papers dealing with this problem, mention should be made of attempts to improve the results by titrating in an ammoniacal medium [3, 4]. Nevertheless, in all these papers, $K_4Fe(CN)_6$ was used as the titrant; the possible effect of other alkali metals present in solution – in addition to potassium – on the titration has not been studied. Convincing proof has been brought forward in some articles to suggest that there is a decrease in solubility of the mixed copper ferrocyanides with decreasing ionic radius of the alkali metal which enters into the composition of the respective precipitates [5-7]. All the same, no studies have been made of a system consisting of Cu^{2+} ions and $Me_4[Fe(CN)_6]$, where Me = Li, Na, K, Rb, Cs. The present article is an attempt to fill this gap.

Determination of the oxidation – reduction potential was carried out on an LP-6 potentiometer, using a platinum indicator electrode and a saturated calomel electrode.

First of all, experiments were carried out in which cupric sulfate solutions containing small amounts of ferricyanide, were titrated with potassium ferrocyanide. For this titration the following amounts were taken: 10 ml of 0.05 M cupric sulfate to which was added 10 ml of 1 N H_2SO_4; water was added to bring the total volume to 50 ml; 0.025 M potassium ferricyanide was added in amounts ranging from one drop to 0.5 ml. Under these conditions formation of a sparingly soluble copper ferricyanide was observed. Titration was carried out with 0.025 M potassium ferrocyanide with careful stirring. The oxidation–reduction potential of the solution changed very little

up to the point where potassium ferrocyanide had been added to the cupric sulfate solution in an amount which was approximately 120% of that required for the formation of a normal copper ferrocyanide $Cu_2[Fe(CN)_6]$. Subsequently, there was observed a scarcely perceptible increase in potential, presumably, as the result of the formation of copper ferrocyanide from the ferricyanide which was obtained on addition of potassium ferricyanide to the cupric sulfate. As a result of this there occurred some increase in the concentration of $[Fe(CN)_6]^{3-}$ ions, and consequently an increase in the oxidation–reduction potential, after which, depending on the amount of potassium ferrocyanide added, there started a comparatively smooth drop in the oxidation–reduction potential.

Thus, these experiments showed that, during titration with potassium ferrocyanide of a cupric sulfate solution to which potassium ferricyanide had been added, there are no sharp changes in the value of the oxidation–reduction potential. Neither was there observed a characteristic jump on the curve for the oxidation–reduction potentials, so that it is impossible to establish exactly the composition of the mixed ferrocyanide of copper and potassium formed. Accordingly, during further work, titration was carried out with a solution of potassium ferrocyanide to which had been added a small amount of potassium ferricyanide. It was assumed, in this case, that there would be observed an increase in the oxidation–reduction potential towards the end of titration, when, presumably, formation of ferrocyanide at the expense of ferricyanide would occur. It was deemed most rational to carry out the titration using a potassium ferrocyanide solution to which 1% of ferricyanide had been added (1% with respect to the ferrocyanide). In such cases a fairly large increase in the oxidation–reduction potential was observed. The cupric sulfate was titrated in acid media. To 10 ml of 0.05 M curpic sulfate was added 10 ml of 2 N H_2SO_4 for preventing formation of basic copper salts. As tests had shown, during titration in a strongly acid medium a more clearly defined potential change can be observed. It is possible that this is determined by an increase in the solubility of copper ferricyanide. It should be noted that during titration in an acid medium, the curve for the oxidation–reduction potentials is located in a higher position than when ordinary solutions are used.

The maximum on the oxidation–reduction potential curve, which corresponds to the highest concentration of ferricyanide ions with respect to $[Fe(CN)_6]^{4-}$ ions is observed, in this case, on addition of about 120% of potassium ferrocyanide with respect to the amount of this compound which is necessary for the formation of the normal copper ferrocyanide. The maximum corresponds to that point at which the copper ions are combined mainly in the form of ferrocyanide and the minimum excess of titrant has been added to the solution. As a result of such an addition, and as a result of the expulsion of $[Fe(CN)_6]^{3-}$ from the precipitate by $[Fe(CN)_6]^{4-}$, there is formed in solution a temporary enhanced concentration of the first type of ions with respect to the latter. On titrating further, the concentration of $[Fe(CN)_6]^{4-}$ increases rapidly, as a result of which the oxidation–reduction potential starts to drop. The maximum on the oxidation–reduction potential curve corresponds to the formation of the mixed ferrocyanide of copper and potassium $K_4Cu_{10}[Fe(CN)_6]$ (or, $5Cu_2[Fe(CN)_6]$. $K_4[Fe(CN)_6]$). The concentration of potassium ions in solution was found to exert some influence on the composition of the mixed copper and potassium ferrocyanide. Thus, on addition of potassium chloride to one of the solutions during titration, there was observed a small shift in the maximum on the oxidation–reduction potential curve towards the formation of a compound containing a larger amount of potassium. In this case 122-125% of the potassium ferrocyanide required for the formation of the normal ferrocyanide was used up for the formation of the mixed ferrocyanide of copper and potassium.

Three series of experiments were carried out in order to clarify the composition of the mixed ferrocyanides of copper with the alkali metals.

In the first series of experiments oxidation–reduction potentials were determined during titration of cupric sulfate with potassium ferrocyanide containing 1% of potassium ferricyanide, rubidium or cesium chloride being added to the solution in amounts equivalent to that of the potassium (Table 1, Fig. 1).

In the second series of experiments the cupric sulfate solution was titrated with sodium ferrocyanide containing 1% sodium ferricyanide, and also containing potassium, rubidium, or cesium chloride in amounts equivalent to that of sodium (Table 2, Fig. 2).

In the third series of experiments, titration was carried out with lithium ferrocyanide containing 1% of lithium ferricyanide, was well as sodium, potassium, rubidium, or cesium chloride in amounts equivalent to that of lithium (Table 3, Fig. 3).

The solutions of lithium and sodium ferrocyanides were prepared from potassium ferrocyanide via lead ferricyanide. Lead ferrocyanide was carefully washed free from potassium and then heated on a water bath with sodium carbonate solution, or with a suspension of lithium carbonate, taken in amounts which were 80% of the equivalent

amount with respect to $Pb_2[Fe(CN)_6]$. The solutions obtained were filtered, and their concentrations established by titration with potassium permanganate in 1 N H_2SO_4. Sodium and lithium ferricyanides were prepared by oxidation of the corresponding ferrocyanides with chlorine water.

TABLE 1

Titration of 10 ml of 0.05 M $CuSO_4$ Solution with 0.025 M $K_4[Fe(CN)_6]$ (containing $K_3[Fe(CN)_6]$) in the Presence of Chlorides of Alkali Metals

a		b		c	
$K_4[Fe(CN)_6]$ In ml	In millivolts	$K_4[Fe(CN)_6]$ + RbCl In ml	In millivolts	$K_4[Fe(CN)_6]$ + CsCl In ml	In millivolts
0,0	725	0,0	730	0,0	730
1,0	750	1,0	750	1,0	750
10,0	755	10,0	750	10,0	750
11,0	765	12,5	765	15,0	755
11,5	790	14,0	795	18,5	770
11,9	820	14,5	850	18,7	785
12,0	825	14,8	870	18,8	850
12,1	825	14,9	870	19,0	915
12,2	795	15,0	875	19,2	940
12,3	790	15,1	860	19,3	950
12,4	770	15,2	850	19,4	900
12,6	660	15,4	680	19,6	755
13,0	600	15,7	640	20,0	725
13,5	585	17,0	615	21,0	685

The results of these experiments are given in Tables 1, 2, and 3 and in Figs. 1, 2, and 3. The amount of the alkali metal ferrocyanide (expressed as a percentage of the amount required for formation of the normal ferrocyanide of copper) is plotted along the abscissa, while the oxidation–reduction potential, in millivolts, is plotted along the ordinate.

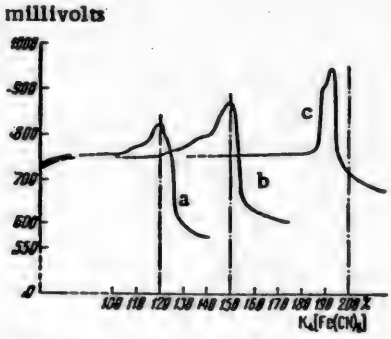


Fig. 1. Change in oxidation–reduction potential during titration of $CuSO_4$ by means of the solutions: a) $K_4[Fe(CN)_6]$; b) $K_4[Fe(CN)_6]$ + + RbCl; c) $K_4[Fe(CN)_6]$ + CsCl.

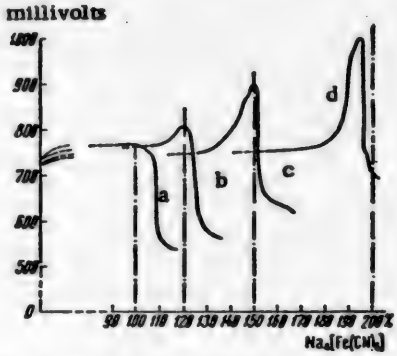


Fig. 2. Change in oxidation–reduction potential during titration of $CuSO_4$ by means of the solutions: a) $Na_4[Fe(CN)_6]$; b) $Na_4[Fe(CN)_6]$ + KCl; c) $Na_4[Fe(CN)_6]$ + + RbCl; d) $Na_4[Fe(CN)_6]$ + CsCl.

In Fig. 1 (curve a) is shown the change in oxidation–reduction potential during titration of cupric sulfate with potassium ferrocyanide. Initially, the curve goes almost parallel to the abscissa; afterwards, towards the end of titration, there is observed some increase in the potential. The potential reaches a maximum and then, comparatively slowly, decreases. During titration with potassium ferrocyanide the maximum is observed after addition of 120-123% of ferrocyanide. On addition to this same solution of potassium ferrocyanide, of rubidium chloride (curve b) and cesium chloride (curve c), in amounts equivalent to the potassium, the highest potential is observed at 150% and

192-193% respectively for ferrocyanide. Addition of sodium and lithium chlorides to potassium ferrocyanide, as was to be expected, has no effect on the position of the maximum on the curve as compared with curve a.

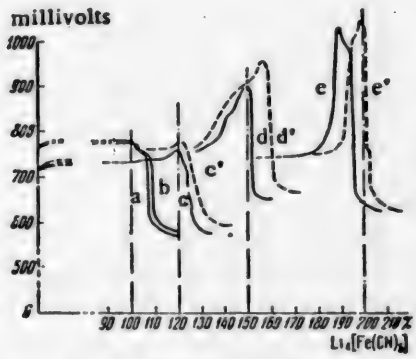


Fig. 3. Change in oxidation–reduction potential during titration of $CuSO_4$ by means of the solutions: a) $Li_4[Fe(CN)_6]$; b) $Li_4[Fe(CN)_6]$ + + NaCl; c and c') $Li_4[Fe(CN)_6]$ + + KCl; d and d') $Li_4[Fe(CN)_6]$ + RbCl; e and e') $Li_4[Fe(CN)_6]$ + CsCl.

In Fig. 2 are shown the curves illustrating changes in the oxidation–reduction potential during titration with sodium ferrocyanide. When only sodium ions were present, the highest potential was observed on addition of 99.8–100% of ferrocyanide (Curve a). On addition of potassium chloride to the sodium ferrocyanide (Curve b), the maximum potential was established on addition of 120-122% of ferrocyanide, i.e., on addition of the same amount of sodium ferrocyanide as during titration with potassium ferrocyanide. During titration with sodium ferrocyanide to which had been added an equivalent amount of rubidium chloride, the maximum potential (Curve c) was observed on addition of 149.4-149.8% of ferrocyanide, i.e., on addition of the same amount of ferrocyanide as that used during titration with potassium ferrocyanide in the presence of rubidium chloride. On addition of rubidium chloride, the potential reached a higher value, while the increase and decrease in potential occurred more sharply than in the case where potassium chloride was added.

Diagram 3 (Fig. 3) was constructed on the basis of the results obtained during titration with lithium ferrocyanide. In this case again, the same regularity was observed in the values of the oxidation–reduction potential as that observed during titration with sodium ferrocyanide. Thus, in the presence of only lithium, or of lithium and sodium, the highest value of the potential was observed on addition of 99.2% of ferrocyanide with respect to the amount necessary for formation of $Cu_2[Fe(CN)_6]$ (Curves a and b). Under these conditions the maximum is poorly defined; the drop in potential proceeds extremely slowly in the presence of excess ferrocyanide.

TABLE 2

Titration of 10 ml of 0.05 M $CuSO_4$ Solution (with 0.025 M $Na_4[Fe(CN)_6]$ containing $Na_3[Fe(CN)_6]$ in the Presence of Alkali Metal Chlorides).

a		b		c		d	
$Na_4[Fe(CN)_6]$ in ml	in millivolts	$Na_4[Fe(CN)_6]$ + KCl in ml	in millivolts	$Na_4[Fe(CN)_6]$ + RbCl in ml	in millivolts	$Na_4[Fe(CN)_6]$ + CsCl in ml	in millivolts
0,0	740	0,0	730	0,0	725	0,0	725
1,0	760	1,0	750	1,0	745	15,0	750
9,9	765	11,0	755	13,0	750	18,0	775
10,0	765	11,5	775	14,0	800	18,5	800
10,1	762	11,8	800	14,5	850	18,8	850
10,2	760	11,9	805	14,8	875	18,9	925
10,3	755	12,0	810	14,9	895	19,0	950
10,5	745	12,1	805	15,0	900	19,1	975
10,6	740	12,2	795	15,1	885	19,2	985
10,7	735	12,3	780	15,2	675	19,3	990
10,8	580	12,4	750	15,3	655	19,4	995
10,9	565	12,5	650	15,4	650	19,5	1000
11,0	560	12,7	625	15,5	645	19,6	750
10,5	540	13,0	575	16,0	635	19,8	720
12,0	525	14,0	560	16,5	625	20,0	700

On addition of potassium chloride (Curve c) the maximum was observed at 120-122%. After the maximum, the potential decreased slowly. On addition of rubidium chloride (Curve d) the maximum was found on the addition of 149.8% ferrocyanide. In this case there was a comparatively large increase in potential while its drop was expressed clearly.

On addition of cesium chloride (Curve e) the maximum was observed at 189-190% with a sharp increase and decrease in the value of the potential. On addition of a large excess of cesium chloride, a shift in the maximum was observed. Thus, on addition of cesium chloride in an amount 2.5 times the equivalent amount of the element with respect to lithium, the maximum value of the oxidation–reduction potential was observed on addition of 198% ferrocyanide (Curve e'). In this latter case cesium chloride was added to the cupric sulfate.

TABLE 3

Titration of 10 ml of 0.05 M $CuSO_4$ with a Solution of $Li_4[Fe(CN)_6]$ (containing $Li_3[Fe(CN)_6]$ in presence of alkali metal chlorides)

a		b		c		d		e		c'		d'		e'	
in ml	in millivolts	in ml	in millivolts	in ml	in millivolts	in ml	in millivolts	in ml	in millivolts	in ml	in millivolts	in ml	in millivolts	in ml	in millivolts
0,0	750	0,0	745	0,0	730	0,0	725	0,0	740	0,0	740	0,0	725	0,0	730
1,0	780	1,0	775	10,0	750	1,0	735	18,0	760	11,5	785	1,0	735	18,0	750
9,9	780	9,0	775	11,5	755	12,5	755	18,5	825	11,7	785	12,5	760	19,1	800
10,0	765	10,0	765	11,7	760	13,5	770	18,6	850	11,9	790	13,5	805	19,2	850
10,1	765	10,1	765	11,8	765	14,0	825	18,7	875	12,0	795	14,5	850	19,3	900
10,2	762	10,2	760	11,9	765	14,5	850	18,8	950	12,1	800	14,5	885	19,4	950
10,3	760	10,3	760	12,0	770	14,7	880	18,9	1025	12,2	800	15,8	905	19,5	1000
10,4	760	10,4	755	12,1	760	14,9	900	19,0	1085	12,3	795	15,5	940	19,7	1010
10,5	755	10,5	750	12,2	725	15,0	900	19,1	955	12,4	785	15,6	955	19,8	1045
10,6	750	10,6	750	12,3	720	15,1	890	19,2	990	12,5	780	15,7	950	19,9	1035
10,7	700	10,7	700	12,4	665	15,2	675	19,3	985	12,6	750	15,8	945	20,0	1025
10,8	615	10,8	620	12,5	650	15,3	660	19,4	980	12,8	700	15,9	925	20,1	1760
10,9	610	10,9	615	12,6	610	15,5	655	19,5	675	13,0	675	16,0	750	20,3	675
11,0	600	11,0	610	13,0	600	16,0	650	19,6	660	13,5	635	16,2	290	20,4	660
11,5	575	11,5	580	14,0	575	17,0	645	20,0	635	14,0	615	17,0	675	21,0	625

The shift in the maximum on the oxidation–reduction potential curve was also observed on addition of excess rubidium chloride. Thus, on addition of rubidium in an amount which was 2.5 times the equivalent amount of this element with respect to lithium, the maximum was observed on addition of 156-158% of ferrocyanide (Curve d').

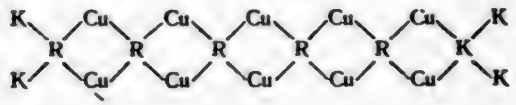
It is necessary to point out that on addition of rubidium chloride to the ferrocyanides of lithium, sodium, and potassium in an equivalent amount, the maximum value of the oxidation–reduction potential was always obtained on addition of ferrocyanide in an amount very near to 150% of the amount required for the formation of $Cu_2[Fe(CN)_6]$.

During formation of the mixed ferrocyanide of copper and potassium, excess of added potassium chloride also led to a displacement of the maximum of the oxidation–reduction potential. Thus, on addition of potassium ions in an amount 2.5 times greater than that equivalent to lithium, the maximum was obtained on addition of about 125% of the ferrocyanide required for formation of $Cu_2[Fe(CN)_6]$. In this case a slower drop in the oxidation–reduction potential was observed during the first period after the maximum (Curve c').

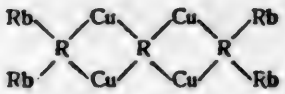
It should be pointed out that the position of the maximum on the oxidation–reduction potential curve during formation of the mixed ferrocyanide of copper and potassium is less stable than in the case of the copper and rubidium ferrocyanide.

It can be concluded from Figs. 1, 2, and 3 that during precipitation of copper salts with lithium or sodium ferrocyanide, the normal copper ferrocyanide is formed $Cu_2[Fe(CN)_6]$.

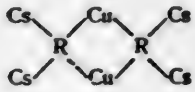
In the presence of potassium ions, since the maximum of the oxidation–reduction potential corresponds to the addition of about 120% of ferrocyanide, the mixed ferrocyanide of copper and potassium is formed $K_4Cu_{10}[Fe(CN)_6]_6$ or written otherwise $5Cu_2[Fe(CN)_6] \cdot K_4[Fe(CN)_6]$. The structure of this salt may be represented as follows:



In the presence of rubidium ions, in the case where this element is added in amounts equivalent to lithium, sodium, or potassium, the maximum is observed on addition of 150% of ferrocyanide; this corresponds to the formation of a mixed ferrocyanide of copper and rubidium $Rb_4Cu_4[Fe(CN)_6]_3$ or $2Cu_2[Fe(CN)_6] \cdot Rb_4[Fe(CN)_6]$:



On addition of a large excess of cesium salts, the maximum oxidation–reduction potential is observed on addition of 200% of ferrocyanide with respect to that necessary for formation of $Cu_2[Fe(CN)_6]$. In this case, obviously, the mixed ferrocyanide $Cs_2Cu[Fe(CN)_6]$:



is formed.

SUMMARY

It has been established that the equivalence point, corresponding to a break or to a maximum on the potentiometric titration curves, depends on the nature of the alkali metal present in solution. During titration with lithium or sodium ferrocyanide, $Cu_2[Fe(CN)_6]$ is formed. In the presence of the ions of the remaining alkali metals mixed ferrocyanides are formed:

$K_4Cu_{10}[Fe(CN)_6]_6$, $Rb_4Cu_4[Fe(CN)_6]_3$ and $Cs_2Cu[Fe(CN)_6]$.

The potentiometric method which shows that greatest possibilities for the determination of copper is titration with rubidium ferrocyanide or titration with the ferrocyanides of the other alkali metals in the presence of rubidium salts.

Received May 29, 1957

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MICROCRYSTALLINE REACTIONS IN MELTS

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An article was published not very long ago [1] in which it was suggested that microcrystalloscopic reactions for certain ions could be carried out by using molten 8-hydroxyquinoline, both as a reagent and as a medium for carrying out the reactions; in the molten drop it is possible to observe crystalline reaction products with copper, zinc, calcium and other salts. Molten 8-hydroxyquinoline has also been used in color reactions for iron and vanadium [2]. Other authors [3] have carried out a color reaction for bismuth with dithizone, using a solution of this reagent in naphthalene for this purpose.

We have tested some reagents dissolved in low melting organic compounds for microcrystalloscopical analytical purposes and have observed some very interesting results. Some reagents, 8-hydroxyquinoline among them, used as media for carrying out microreactions, did not prove suitable. With such reagents it was only possible to work at temperatures higher than their melting points. On cooling below this temperature, the material crystallized rapidly, and the crystals of the solvent itself (the medium) prevented observation of the crystalline reaction products.

TABLE

Dimensions of Nickel Dimethylglyoximate Crystals

Nickel content of test sample, in γ	Solvent	
	Benzophenone	Aqueous ammonia solution
	Maximum dimensions of the crystals, in μ	
1	1000	30
0.5	600	30
0.1	400	25
0.05	150	20
0.025	50	15

We used reagents dissolved in molten benzophenone (m.p. 48°) or salol (m.p. 42°). The use of salol, and, particularly benzophenone, proved to be very convenient because of their capacity to supercool. A molten drop, containing reagent and reaction product, retained its liquid state on cooling to room temperature, and remained in that state for a long time. We succeeded in keeping preparations in benzophenone in a liquid state over periods of 5-6 days; in individual cases considerably longer; in the case of salol the preparations remained liquid for only 24 hours.

Detection of nickel with dimethylglyoxime was carried out as follows. 2 mg of dimethylglyoxime was dissolved in 1 g of molten benzophenone or salol and the solution transferred to a mortar. After cooling, a small crystal of benzophenone (or salol) was added for seeding; the mass thereupon solidified rapidly; it was then ground to a powder. A drop of a solution of a nickel salt was heated on a microscope slide to evaporate the water. To this dry residue was added a few grains of the solution of diemthylglyoxime in benzophenone (or salol) and the

whole heated to the molten state. After a few minutes the slide was examined under the microscope. When these conditions were used, red, very large, and well-formed crystals of nickel dimethylglyoximate could be observed. (Fig. 1).* The crystal size gradually increased. When nickel was detected in aqueous or aqueous-ammoniacal media, the crystals obtained were almost invariably considerably smaller (see Table).

The crystals formed in salol were smaller than those obtained in benzophenone.

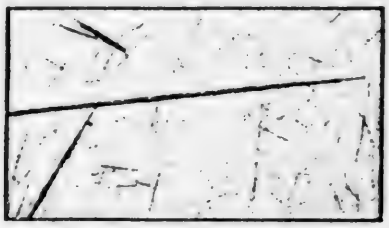

Fig. 1. Nickel dimethylglyoximate crystals (solvent—benzophenone).

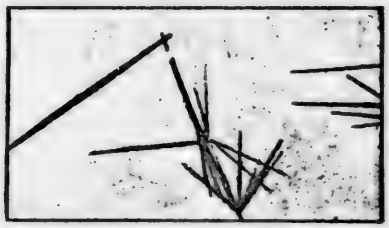

Fig. 2. Nickel α-benzyldioximate crystals (solvent—benzophenone).

Fig. 3. Crystals of $C_9H_7N \cdot H[BiI_4]$ (solvent—diphenylamine).

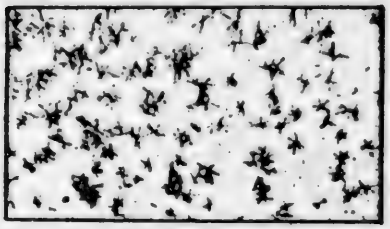

Fig. 4. Crystals of $C_9H_7N \cdot H[BiI_4]$ (solvent — water).

Using α-benzyldioxime in a benzophenone medium we were abie to obtain with nickel salts, large, bright--red, needles with particle sizes amounting to 300 μ in length (Fig. 2). Next we investigated a number of microcrystalloscopic reactions for bismuth, based on the formation of the compound $BH[BiI_4]$ (where B is a base), characterized by an intense color, and often recommended for detection of bismuth [4]. The reagent was a solution of a suitable base and ammonium iodide in a readily fusible organic compound. When this reaction was carried out using ammonium iodide, the results obtained were unsatisfactory. Only by using quinoline diethylate ($C_9H_7NC_2H_5$) dissolved in molten diphenylamine (m.p. 53.5°) was it possible to detect bismuth clearly. 2 mg of the reagent indicated was dissolved in 1 g of molten diphenylamine; after cooling and solidifying the solid solution was ground to a powder. The reagent was placed on, and fused on, the still moist residue obtained on a microscope slide by evaporation of a drop of a bismuth salt. Dark-red crystals 200-300 μ long were obtained (Fig. 3). These crystals could readily be observed even in those cases where the diphenylamine itself crystallized during cooling. The crystals obtained in aqueous media were no longer than 50-60 μ (Fig. 4). Replacement of diphenylamine by benzophenone or salol led to the formation of small crystals. Lead salts reacted with quinolinediethylate dissolved in diphenylamine to give reaction products in the form of almost colorless needles up to 150 μ long.

SUMMARY

The use of certain organic reagents dissolved in molten, indifferent organic compounds, leads, in a number of cases, to the formation of large crystals. Microcrystalloscopic reactions for nickel are described in which nickel reacts with dimethylglyoxime and α-benzyldioxime respectively, in a medium of molten benzophenone; reactions are also described for detecting bismuth and lead, using quinolinediethylate in a medium of molten diphenylamine.

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* All the micro-photographs were obtained using a magnification of 150.

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THE APPLICATION OF DIPHENYLCARBAZONE FOR THE PHOTOMETRIC DETERMINATION OF COPPER IN IRON AND STEEL

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A number of photometric techniques have been proposed in recent years for the determination of copper in iron and steel [1-9]. However, many of them require reagents which are not readily available, or special apparatus, and this limits the possibilities of their practical application. Our observations have shown that, compared with the techniques described, a much more convenient method for the microdetermination of copper, is a very sensitive test based on the interaction of copper with diphenylcarbazone to form a complex which is sparingly soluble in water. Hydrogen ion concentration has a considerable effect on the formation of the complex: the optimum conditions for carrying out the reaction lie within the pH limits 4-5.

The copper derivative of diphenylcarbazone is insoluble in water, and only sparingly soluble in amyl alcohol, ether, and carbon tetrachloride; it dissolves readily in benzene and its homologs. The red solutions of the complex conform to the Lambert-Beer law.

Under the conditions indicated, diphenylcarbazone does not form benzene-soluble compounds with WO_4^{2-} the following ions: Ag^+, $AuCl_4^-$, Zn^{2+}, Al^{3+}, Sn^{2+}, $V_2O_7^{4-}$, Sb^{3+}, Bi^{3+}, WO_4^{2-}, F^-, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, UO_2^{2+} Ni^{2+}, Cr^{3+}, $PtCl_6^{2-}$, $B_4O_7^{2-}$, Ti^{4+}, Tl^+.

With mercury, diphenylcarbazone only reacts in the same way as copper when chlorides are absent; while diphenylcarbazone reacts with molybdenum, cadmium, and lead at high concentrations of these metals which exceed the copper content several thousand times.

The reaction is very sensitive and permits detection of tenths of a microgram of copper.

In developing a quantitative method of determining copper in steel and iron by means of the reaction described, it was necessary, in the first instance, to resolve the problem of getting a completely transparent solution during the extraction of the copper-diphenylcarbazone complex with benzene, since the presence of even the slightest turbidity leads to a considerable experimental error as the result of the partial adsorption of the copper complex by this turbidity.

Another undesirable feature proved to be precipitation of iron as hydroxide which possesses a similar adsorptive capacity with respect to copper ions [10-12].

Necessary Reagents. An alkaline solution of phenolphthalein; this was prepared by weighing out 10 mg of phenolphthalein on a torsion balance and transferring it to a flask, to which was then added 1 ml of concentrated ammonia solution and 9 ml of twice distilled water. This solution was prepared daily. 2) A benzene solution of diphenylcarbazone * was prepared as follows; 10 mg of diphenylcarbazone was weighed out on a torsion balance and carefully placed in a 100 ml standard flask; 20-25 ml of benzene was added and the flask then placed in a beaker of hot water until complete solution of the crystals had been attained. The flask was then cooled and benzene added to bring the volume up to the mark; 0.4 ml of pyridine was finally added to accelerate the rapid

* The commercial grade of diphenylcarbazone marked as analytical grade material could not be used without the preliminary treatment with potassium hydroxide and H_2O_2 described in L. M. Kul'berg's book, "Syntheses of Organic Reagents for Inorganic Analysis," Goskhimizdat, Moscow-Leningrad, 1947, p. 68.

formation of the copper complex.

Analytical Procedure. 100-250 mg of test material was weighed out on an analytical balance and transferred to a 100 ml Kjeldhal flask made of heat-resistant glass. 4 ml of twice-distilled water and 1 ml each of concentrated sulfuric and nitric acids were then added to the contents of the flask; then working with sparingly soluble samples of steel, 1 ml of concentrated hydrochloric acid was also added. The sample was dissolved by careful heating. On cooling, 0.5 ml of hydrogen peroxide was added and the contents of the flask heated until liberation of gas bubbles ceased.

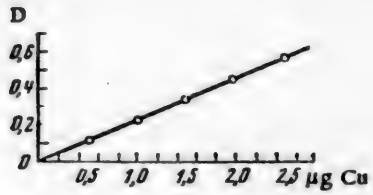

Fig. 1. Calibration curve. Filter S 53; layer thickness 10 mm.

1 ml each of concentrated sulfuric and nitric acids was added to the cooled contents of the flask, and the whole quantitatively transferred to a 250 ml standard flask; the volume was finally made up to the mark with water.

The copper content of the test material was established by measuring out 2 ml of the solution from the 250 ml flask into another Kjeldhal flask using a pipet with two marks on it; 0.2 g of a univalent metal phosphate was added to this aliquot and the whole shaken. After the salts had dissolved 0.5 ml of the alkaline phenolphthalein solution was added. To this same flask was added concentrated ammonia in an amount equal to twice the volume required to neutralize the acid in the test liquid. The slightly turbid solution was shaken until the turbidity had completely disappeared; the solution was then neutralized with a saturated solution of potassium dihydrogen phosphate which was added carefully from a buret. After this, the volume of water which it was necessary to add to bring the total volume of the liquid in the flask to 15 ml was calculated.

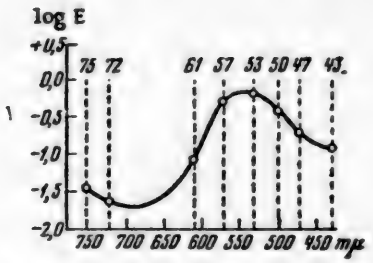

Fig. 2. Curve for the absorption of a solution of the copper-diphenylcarbazone complex in benzene.

When, during neutralization of the solution, a large volume of phosphate has to be used — this can happen as a result of the lowered solubility of the salt at a low temperature — in order to avoid increasing the volume to a value greater than 15 ml, it was found necessary to add about 0.5 g of crystalline phosphate first, and then add the requisite amount of reagent from a buret.

To the completely clear solution treated in this way was added 5 ml of the benzene solution of diphenylcarbazone and the whole shaken thoroughly; after the layers had separated the benzene layer was transferred to a 5 or 10 mm photometer cell, depending on the intensity of the benzene layer. The adsorption was measured using a S 53 filter. The reference liquid placed in the other photometer cell was the solution of diphenylcarbazone in benzene used for extracting the copper.

The calibration curve was constructed by using a standard cupric sulfate solution containing 10 μg of copper per ml; during preparation of this solution, in order to prevent formation of basic salts, 10 ml of 10% sulfuric acid solution was added per 500 ml of liquid, after which the volume was made up to the mark with water. Having measured out aliquots of the standard solution into Kjeldhal flasks by means of a microburet, such that after making up to volume in 250 ml standard flasks, 2 ml of these final solutions contained 1, 2, 3, etc. μg of copper, the procedure outlined above for determination of copper in steel was followed. In order to promote more uniform boiling of the liquids in these cases, it was found necessary to add 2-3 glass beads to the contents of the Kjeldhal flasks. Furthermore, when determinations were made it was found essential to carry out a blank, since the reagents and water used in the work always contained copper.

Having measured the density of the solutions, a calibration curve was constructed (Fig. 1).

The absorption curve is shown in Fig. 2.

DISCUSSION OF RESULTS

In view of the exceptional sensitivity of the reaction, whereby it is possible, using a photometer, to detect hundredths of a microgram of copper, it is essential to treat the flasks, etc. used in the work, in order to avoid contamination with traces of copper, which will affect the results considerably. For this purpose it is recommended therefore that the flasks be washed with hot sulfuric acid, followed by hot concentrated ammonia; they are washed then several times with tap water, and finally, rinsed with twice-distilled water. Subsequently, in the course of the work, the flasks are washed several times with tap water, and twice with twice-distilled water.

TABLE 1

Results of Replicate Determinations of the Amount of Copper in the Same Sample of Test Material

Test material	Copper content, in %			Mean value
	I	II	III	
Stainless steel				
Sample I	0.207	0.205	0.209	0.207
Sample II	0.845	0.838	0.846	0.843
Instrumental steel				
Sample I	0.159	0.159	0.158	0.158_7
Sample II	0.132	0.134	0.134	0.133_3
Sample III	0.127	0.127	0.127	0.127
Sample IV	0.235	0.235	0.236	0.235_3
Iron				
Sample I (wire)	0.075	0.074	0.074	0.074_3
Sample II (sheet)	0.178	0.175	0.174	0.176
Sample III (wire)	0.092	0.095	0.092	0.093

All the solutions used in the course of the work should be prepared using twice-distilled water prepared in a glass distillation apparatus. The hands of the operator should not come in contact with any copper materials; balances with copper weighing pans should not be used either.

TABLE 2

Determination of Copper After Addition of Various Amounts of it to a Sample of Test Material

Test material	Copper content of the solution taken for analysis in μg	Amount of copper added to 2 ml of test solution, in μg	Calculated amount of copper, in μg	Amount of copper found, in μg	Error, in %
Stainless steel					
Sample I	4.015	0.5	4.515	4.7	+4.3
Sample II	15.848	1.0	16.848	16.780	−0.5
Sample III	5.193	3.0	8.193	8.171	−0.3
Sample IV	3.422	0.5	3.922	3.93	+0.2
Sample IV	3.216	1.0	4.216	4.191	−0.6
Iron					
Sample II (sheet)	2.05	1.2	3.25	3.33	+2.4
Sample II "	3.67	0.7	4.37	4.45	+1.8
Sample II "	1.66	2.0	3.66	3.50	−4.4
Sample II "	2.09	0.5	2.59	2.63	+1.5

In order to establish the reproducibility of the results obtained during determination of copper in the same test material, we carried out a series of tests of which the results are given in Table 1.

In order to establish the accuracy of the method, a series of experiments was carried out in which known amounts of copper were added to the test material (Table 2).

As the results given in Table 2 show, the experimental error does not exceed 4%.

A very important stage in this method is the complexing of iron as a soluble complex by addition of excess ammonia and sodium phosphate to the solution. This technique possesses several advantages over the technique of precipitating iron as the hydroxide, since it is possible by using the former, to obtain completely clear and colorless solutions which do not interfere with complete extraction of the copper complex.

In order to establish the amount of copper absorbed by precipitated ferric hydroxide when the normal technique is used, the following experiment was carried out. After a sample of steel had been dissolved and iron had been precipitated by means of ammonia, 100 ml of which was added, the amount of copper in the filtrate, whose volume had been made up to 250 ml, was found to be 0.1877%. The precipitate of ferric hydroxide, freed from solution by decanting and centrifuging, was quantitatively transferred to a Kjeldahl flask; after dissolution in a mixture of nitric and sulfuric acids, the solution was transferred to a 250 ml flask and precipitated again with 100 ml of concentrated ammonia. When this was done, another 0.0084% of copper was found. On precipitating for a third time only traces of copper were found. Thus, the total content of copper in the sample of steel taken was found to be 0.1961%. Determination of copper in the same sample of steel by the method we have suggested above gave a value of 0.207%.

By means of appropriate modification the method could be used for the "in situ" determination of copper in iron and steel.

SUMMARY

A method has been developed for the photometric determination of copper in iron and steel, using diphenylcarbazone. The copper derivative of diphenylcarbazone is insoluble in water but is readily extracted by benzene and its homologs; the intensity of the red benzene extract conforms to the Lambert-Beer law. The reaction described is specific and highly sensitive. It permits detection of tenths of a microgram of copper. Iron is complexed as a phosphate complex. The experimental error for the determination of copper in iron and steel does not exceed 4%.

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THE POSSIBILITY OF USING MUREXIDE AS A REAGENT FOR THE PHOTOMETRIC DETERMINATION OF ZINC

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Comparatively few good reagents are known for the photometric determination of zinc. Thus, dithizone, 8-hydroxyquinoline, and some other materials have found practical application for this purpose [1]. Dithizone and 8-hydroxyquinoline have been recommended as the best reagents, but they are not free from some drawbacks [2]. A possible reagent for the photometric determination of zinc is murexide (ammonium purpureate) which has recently found wide application in complexometry [3, 4]. Results have been given on the use of murexide for the photometric determination of calcium [5-9] while simple methods have been developed for synthesizing murexide [10], and for stabilizing its solutions [11] etc.

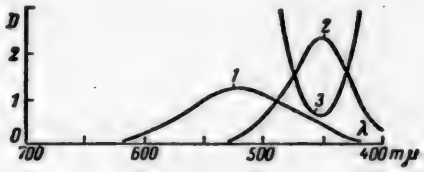

Fig. 1. Absorption curves for murexide (1), and its complex with zinc (2), and for light filter No. 7 with photometer FM (3).

Murexide interacts with the ions of many metals [5, 6, 12, 13] although in this connection the results are contradictory, for example with respect to the ions UO_2^{2+}, Th^{4+}, and Pb^{2+} [12-13]. The instability constants of many of the complexes formed have been determined [12]. A detailed study of the interaction of murexide with zinc ions, which one of us carried out in conjunction with Vestfried [14], has shown that purpuric acid forms a stable complex $Zn(H_3R)_2^{2-}$, whose instability constant is $K = 4.8 \cdot 10^{-10}$. It is essential that the absorption band for the complex (λ_{max} = 455 mμ) should be displaced appreciably with respect to the absorption band for murexide itself (λ_{max} = = 520 mμ), as is evident from Fig. 1. The reaction of murexide with zinc ions is very sensitive. The molar absorption coefficient of the complex ϵ_{max} amounts to 40,000.

It was of interest to establish the possibility of using murexide for the direct photometric determination of zinc. The murexide necessary for the work was synthesized from uric acid [15]. The finished product was carefully washed free from alloxantin by means of absolute ethanol. Aqueous murexide solutions were prepared in twice-distilled water. Purified zinc sulfate which had been analyzed gravimetrically was used as the source of zinc ions. A spectrodensograph [16] as well as an FM photometer (vertical model) were used for carrying out photometric measurements of the solutions; for greater convenience the FM photometer was fixed in a horizontal position so that it was possible to use cells from the FEK-M photocolorimeter.

During measurements of the optical density over the range 0.5-0.8 in the FM photometer using a No. 5 filter (maximum transmission at λ_{max} = 525 mμ) the relative error did not exceed 0.6-0.7%, while on using a No. 7 filter (λ_{max} = 455 mμ), the error increased to 1.2-1.5%.

Murexide solutions, particularly in acid and alkaline media, are unstable with time. According to our results, at a pH from 6 to 8 it is possible to use solutions over a period of several hours, so that we always used freshly prepared solutions. The stability of murexide solutions when the latter are buffered increases slightly. In the presence of zinc ions the optical density of the solutions remains almost constant for 30-45 minutes. This period is quite sufficient for carrying out photometric measurements.

The optical density of solutions containing zinc ions and murexide is strongly dependent on the pH of the medium. For a ratio of the concentration of zinc ions to murexide of 1 : 6, the maximum optical density was observed at a pH of 10.5 (Fig. 2). Measurements were carried out on spectrodensograph at 460 mμ. The concentrations of the zinc ions (c_{Zn}) and murexide (c_R) were $4.2 \cdot 10^{-5}$ and $2.5 \cdot 10^{-4}$ mole/liter. The necessary pH was established by addition of hydrochloric acid or sodium hydroxide to mixtures of the original solutions. A similar curve was also obtained on using buffer solutions. As is evident from Fig. 2, the reaction is most sensitive at pH 10-11; however, the stability of the solutions with time decrease considerably. In this connection, in further work we worked at pH 7.5, which was established by means of a veronal buffer [17].

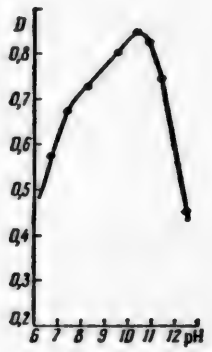

Fig. 2. Change in the optical density of solutions of the complex formed between zinc and murexide at various values of the pH of the medium.

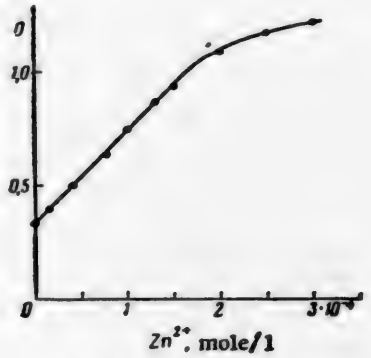

Fig. 3. Calibration curve. Photometer FM; light filter No. 7; thickness of layer in the cell 0.5 cm.

The calibration curve is shown in Fig. 3. The solutions were prepared by mixing equal volumes (10 ml each) of murexide solution (at a constant concentration of $c_R = 2.25 \cdot 10^{-3}$), buffer solution (with a pH of 7.5) and zinc sulfate (different concentrations). Optical density was measured within 5-7 minutes of mixing the solutions. The maximum concentration of zinc ions in the mixture amounted to $3 \cdot 10^{-4}$ mole/liter for a constant murexide concentration of $7.5 \cdot 10^{-4}$ mole/liter. As can be seen from Fig. 3., Beer's law is followed quite well up to a zinc concentration of $1.5 \cdot 10^{-4}$ mole/liter, i.e., up to a ratio of $c_R : c_{Zn} \geq 5$. Measurements were carried out with respect to a colorless glass plate fitted into the second beam of the apparatus; as a result of this the curve did not pass through the origin. Determination of zinc was found to be possible at concentrations as low as $2 \cdot 10^{-5}$ mole/liter. The reaction sensitivity can be increased by using longer cells and higher pH values.

TABLE 1

Reproducibility of the Determination of Zinc by Means of Murexide

Test No.	$c = 3.0 \cdot 10^{-4}$		$c = 7.5 \cdot 10^{-4}$		$c = 1.3 \cdot 10^{-3}$	
	D	$c \cdot 10^4$	D	$c \cdot 10^4$	D	$c \cdot 10^4$
1	0,47	3,1	0,64	7,4	0,85	1,27
2	0,45	2,9	0,65	7,5	0,88	1,32
3	0,47	3,1	0,64	7,4	0,86	1,28
4	0,47	3,1	0,66	7,8	0,87	1,30
5	0,45	2,9	0,64	7,4	0,87	1,31
6	0,46	3,0	0,65	7,5	0,86	1,28
7	0,47	3,1	0,66	4,8	0,87	1,30
$\bar{c}$	$(3,03 \pm 0,09) \cdot 10^{-4}$		$(7,5 \pm 0,17) \cdot 10^{-4}$		$(1,29 \pm 0,02) \cdot 10^{-3}$	
δ	3%		2,3%		1,5%	

In order to evaluate the reproducibility of the method, replicate determinations of zinc were carried out at three different concentrations. The solutions were prepared as indicated above. From the results given in Table 1 it is evident that the relative error (δ %) for the determination of mean values of c_{Zn} does not exceed ± 3%. Calculations were made at a confidence level of α = 95%. [18].

TABLE 2

Effects of Certain Metals on the Determination of Zinc (initial concentration of zinc – $c_{Zn} = 5 \cdot 10^{-5}$ M)

Test No.	Cu		Cr		Al			
	$c \cdot 10^5$	D	$c \cdot 10^5$	D	$c \cdot 10^5$	D	$c \cdot 10^5$	D
1	0,0	0,390	0,0	0,388	0,0	0,390	0,0	0,470
2	1,0	0,389	0,3	0,386	1,0	0,385	1,0	0,468
3	5,0	0,405	1,0	0,370	5,0	0,388	5,0	0,466
4	10,0	0,460	—	—	10,0	0,386	10,0	0,467
5	16,0	0,515	—	—	25,0	0,335	20,0	0,465
6	—	—	—	—	45,0	0,323	50,0	0,466
7	—	—	—	—	—	—	60,0	0,451
pH	7,3		7,3		7,3		10,3	

Thus, experiments with pure solutions of zinc sulfate showed that murexide actually behaves as a very sensitive reagent for zinc ions, and can be used for its photometric determination. All the same, because of the low selectivity of murexide, difficulties may arise when attempts are made to use it for the determination of zinc in actual test materials.

The possibility of using murexide for the photometric determination of zinc was considered from the point of view of analyzing aluminum alloys containing approximately 10% zinc, 3% copper, 0.5% chromium, and 86-87% aluminum. In order to check on interference from copper, chromium, and aluminum during determination of zinc with murexide, solutions were prepared with a constant zinc concentration ($5 \cdot 10^{-5}$ M) and variable amounts of the foreign metals (Table 2). For this purpose 10 ml of $9.0 \cdot 10^{-4}$ M murexide solution was mixed with 5 ml of buffer solution, 10 ml of $1.5 \cdot 10^{-4}$ M zinc sulfate, and 5 ml of the solution (with varying concentrations) of the corresponding metal sulfate. Table 2 contains the results obtained for the optical density of the solutions; it is clear from these results that at pH 7, aluminum in an amount twice that of zinc, cannot be tolerated (the solutions become turbid on account of the formation of the hydroxide), while the permissible limit for copper or chromium (taken separately) is not more than one fifth of the amount of zinc. By working at a pH > 10, aluminum in amounts which are ten times that of the zinc can be tolerated, since, under these conditions, the hydroxide dissolves. The results obtained show that by using an alkali method for dissolving the aluminum alloys, and then removing the non-amphoteric hydroxides, it is possible to determine zinc in the presence of a large amount of aluminum. In alloys of the type considered above, the ratio of Cr to Zn is approximately 1 : 20, which is considerably less than the permissible limit (1 : 5, as can be seen from Table 2); consequently, the presence of chromium in an alkali solution will not interfere with zinc determination.

SUMMARY

1. The possibility of using murexide for the photometric determination of zinc has been investigated.

2. Experiments have shown that at pH 7.5, solutions conform to Beer's law at zinc concentrations up to $1.5 \cdot 10^{-4}$ mole/liter, when the murexide concentration of the solution is $7.5 \cdot 10^{-4}$ mole/liter.

3. Determination of zinc is possible at a concentration of $2 \cdot 10^{-5}$ mole/liter. On increasing the pH to 10-11, the sensitivity of the reaction increases considerably.

4. The effect of copper, chromium, and aluminum (which accompany zinc in certain aluminum alloys) on the photometric determination of zinc by means of murexide has been studied.

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H-RESORCINOL AS A REAGENT FOR THE PHOTOMETRIC DETERMINATION OF BORIC ACID

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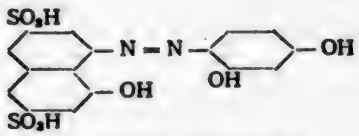
The hydroxyanthraquinones alizarin, quinalizarin, carminic acid and others containing the hydroxyl group in the para position with respect to the quinone group have been used for the photometric determination of boric acid. Brightly colored solutions of these hydroxyanthraquinones in concentrated sulfuric acid, on addition of boric acid, change their color.

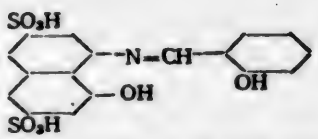
Other organic compounds containing a hydroxyl group adjacent to the carbonyl group, e.g., resacetophenone [1], and the dye chromotrope 2B [2] in the tautomeric hydrazo-form, also react with boric acid in sulfuric acid medium.

In other methods the reaction of boric acid with the dibenzoyl methane derivative curcumin has been used. Dyes which are salicylic acid derivatives behave in a similar way to curcumin on evaporating their acid solutions; the reaction sensitivity is, however, low [3].

In contrast to these color reactions which are carried out in concentrated sulfuric acid, or by removing water by evaporation, reactions have been found which can be carried out in weak acetic acid solutions [4]. Compounds containing two hydroxyl groups in adjacent para- and ortho-positions to the azo- or azomethine group can act as reagents:



H-resorcinol (8-hydroxy-3,6--disulfonaphthalene < 1-azo-1'> > −2', 4'-dihydroxybenzene)



The azomethine derived from H-acid and salicaldehyde

On carrying out the reaction with the azo dye derived from diazotized H-acid and resorcinol, the color of the solution changes from yellow to rose, while the second compound − azomethine − gives a bright-yellow color in acetic acid solutions of boric acid. It has been shown [4-5] that both of these reagents can be used for the photometric determination of boron.

We set out to study the composition and properties of the compound formed between boron and the dye H--resorcinol, and to determine the dissociation constant, the molar extinction coefficient, the effect of the pH of the solution, and the time for complete formation of the compound.

Composition of the Compound formed between H-resorcinol and Boric Acid. In order to determine the stoichiometric ratio between boric acid and H-resorcinol in the compound formed by them, using the method of "continuous variation" [6], stock 10^{-3} M solutions of boric acid and H-resorcinol were prepared (H-resorcinol − − 0.044%, boric acid − 0.0062%). The solutions were acidified with 1 N acetic acid:

Into a series of 50 ml standard flasks were pipetted various amounts of boric acid and reagent, the amounts taken being such that the total final volume in each case was 5 ml. The procedure followed was to pipet the boric acid solution into a flask first; this was then diluted to 25-30 ml, 5 ml of acetic acid was then added by means of a pipet; the H-resorcinol was next added and the volume made almost up to the mark with water. The solutions were heated on a water bath to approximately 95° for 5-10 minutes; the flasks were then cooled and the volume made up the mark, the flasks were finally allowed to stand for 24 hours. The light absorption of the solutions was measured on a type FM universal photometer using a M-53 filter (maximum transmission at 530 mμ).

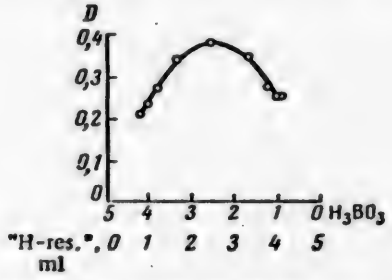


Fig. 1. Determination of the composition of the compound formed between boric acid and H-resorcinol.

The light absorption was measured as follows: into one 50 mm cell was introduced the test solution of boric acid plus reagent, while into the other was introduced a solution containing the same amount of boric acid.

The results obtained were the means of three readings.

As is evident from Table 1 and Fig. 1, the maximum light absorption is observed at a ratio of 1 : 1 of the volumes of boric acid to reagent. This means that in the compound formed there is one molecule of boric acid per molecule of H-acid. This confirms the formula suggested previously for this compound of boric acid with H-resorcinol.

Dissociation Constant of the Compound Formed Between Boric Acid and H-Resorcinol in Solution

In order to determine the dissociation of the boric acid – H-resorcinol complex, measurements were carried out at three pH's, namely 2.2, 2.6, 3.0. The requisite hydrogen-ion concentration was established by means of a hydrogen phthalate buffer; for the preparation of the latter, solutions of 0.5 M HCl and 0.4 M potassium hydrogen phthalate were used. A pH of 2.2 was obtained by adding 6.25 ml of potassium hydrogen phthalate and 4.7 ml of HCl, and pH of 2.6 by addition of 3.3 ml HCl and 6.25 ml phthalate; a pH of 3.0 was obtained by using 2.03 ml of HCl and 6.25 ml of phthalate; these were the amounts required for the final 50 ml of solution. The amounts of hydrogen phthalate and hydrochloric acid taken correspond to the composition of the buffer mixtures required for these pH values [7].

TABLE 1

Determination of the Composition of the Boric Acid – H-Resorcinol Complex

Vol. H_3BO_3 : : Vol. reagent	Amount, in ml		Optical density	
	H_3BO_3 10^{-3} M	H-resorcinol 10^{-3} M	1st series	2nd series
5 : 1	4,17	0,83	0,232	0,232
4 : 1	4,00	1,00	0,242	0,245
3 : 1	3,75	1,25	0,283	0,290
2 : 1	3,34	1,66	0,350	0,370
1 : 1	2,50	2,50	0,388	0,387
1 : 2	1,66	3,34	0,360	0,370
1 : 3	1,25	3,75	0,280	0,282
1 : 4	1,00	4,00	0,262	0,265
1 : 5	0,83	4,17	0,260	0,260

The dissociation constant K was determined by measuring the light absorption of four series of solutions: the first solution contained 2.5 ml each of the 10^{-3} M solutions of H-resorcinol and boric acid in a total volume of 50 ml. The final concentration of each of the components thus amounted to $(2.5 : 50) \cdot 10^{-3} = 5 \cdot 10^{-5}$ M. The light absorption of this solution was a measure of the amount of the compound formed for a ratio of H-resorcinol to boric acid of 1 : 1. (see Table 1); the first, second and third columns in the table correspond to solutions containing boric acid in amounts which were 20, 40, and 60 times greater than the amount of the acid in the first solution; the amount of H-resorcinol was the same. The value of the light absorption of each of these solutions was found to be proportional to the amount of the compound formed by complete complexing of the components, since in the presence of boric acid the dissociation of the compound should be suppressed. Varying excess amounts of boric acid were taken (20-60 times the amount in the first experiment) for controlling completeness of the suppression of dissociation.

$K_{dissoc.}$ was calculated as follows: from the equation H_3BO_3 + H-resorcinol = B · H-resorcinol.

$$K_{dissoc.} = \frac{(H_3BO_3) \cdot (\text{H-resorcinol})}{(\text{BH-resorcinol})}$$

if one denotes the light absorption of solution 1 with the equilibrium concentration of components by ϵ; while ϵ_{max} denotes the light absorption of a solution in which the dissociation of the complex is suppressed, and the original concentration of the components is $5 \cdot 10^{-5}$ M, then $(\text{BH-resorcinol}) = \frac{\epsilon}{\epsilon_{max}} \cdot 5 \cdot 10^{-5}$; $[H_3BO_3] =$ $= [\text{H-resorcinol}] = 5 \cdot 10^{-5} \cdot \left(1 - \frac{\epsilon}{\epsilon_{max}}\right)$

$$\text{from which } K_{dissoc.} = \frac{5 \cdot 10^{-5}\left(\frac{\epsilon_{max} - \epsilon}{\epsilon_{max}}\right) \cdot \left(\frac{\epsilon_{max} - \epsilon}{\epsilon_{max}}\right)}{\frac{\epsilon}{\epsilon_{max}}} = \frac{(\epsilon_{max} - \epsilon)^2}{(\epsilon_{max} \cdot \epsilon)} \cdot 5 \cdot 10^{-5}.$$

When the degree of dissociation $\frac{\epsilon_{max} - \epsilon}{\epsilon_{max}}$ is denoted by α, then $\frac{\epsilon}{\epsilon_{max}} = 1 - \alpha$, and the equation for the dissociation constant assumes the form:

$$K_{dissoc.} = \frac{\alpha^2}{1 - \alpha} 5 \cdot 10^{-5}$$

The experimental values are given in Table 2.

TABLE 2

Determination of the Dissociation Constant of the Compound Formed Between H-Resorcinol and Boric Acid

pH of the solution	Optical density ϵ mean from 3 experiments						
	I 1 : 1 H-resorcinol to H_3BO_3	II 1 : 20	III 1 : 40	IV 1 : 60	Mean II, III, IV ϵ_{max}	α	$K_{dissoc.}$
2,2	0,258	0,739	0,748	0,744	0,744	0,653	$6,15 \cdot 10^{-5}$
2,6	0,259	0,755	0,771	0,766	0,764	0,661	$6,42 \cdot 10^{-5}$
3,0	0,259	0,761	0,771	0,759	0,764	0,661	$6,42 \cdot 10^{-5}$
Mean	0,259	0,752	0,763	0,756	0,757	0,658	$6,33 \cdot 10^{-5}$

Since the value for the light absorption is almost the same for experiments II, III, and IV, thus testifying to suppression of the dissociation constant already at a 20-fold excess of boric acid, it was found possible to take the

mean value from the experiments for calculating α. Both the degree of dissociation α, as well as $K_{dissoc.}$ are independent of pH at 2.2-3.0. Accordingly it was found possible to take the mean value from a series of experiments carried out at various pH's.

Calculation of the molar extinction coefficient was carried out on the basis of the mean value of ϵ_{max} corresponding to complete formation of the compound.

The mean value of ϵ_{max} was 0.757 from which the molar extinction coefficient at 530 mμ was found to be equal to:

$$E = \frac{\epsilon^{mean}_{max}}{c \cdot 1} = \frac{0.757}{5 \cdot 10^{-5} \cdot 5} = 3028.$$

where c is the concentration in mole/liter; 1 is the length of the cell in cm.

The values of the molar extinction coefficient in separate experiments were:

$$E_I = \frac{0.744}{5 \cdot 10^{-5} \cdot 5} = 2976. \qquad E_{II} = \frac{0.764}{5 \cdot 10^{-5} \cdot 5} = 3056.$$

Conditions for Carrying out the Reaction During the Photometric Determination of Boron. A large excess of H-resorcinol should not be taken, since the solution of the reagent itself exhibits considerable light absorption in the the same wave-length region as that used for measuring the light absorption of the H-resorcinol – boric acid complex (530 mμ). Accordingly, we carried out some tests with the aim of establishing the maximum possible amount of reagent, in the presence of which the light absorption of the complex could be conveniently measured.

TABLE 3

Choice of the Amount of Reagent

Amount of reagent, in ml	Value of the extinction immediately after adding the reagent		Value of the extinction after 24 hours	
	Solution of H-resorcinol and H_3BO_3	Blank test	Solution of H-resorcinol and H_3BO_3	Blank test
2.5	0.316	1.20	0.481	1.21
5.0	0.438	1.73	0.609	1.75
8.0	0.481	2.40	0.653	2.45
10.0	0.629	2.60	0.683	2.68

Solutions were prepared such that 50 ml of the solution contained 2.5 ml of 10^{-3} M H_3BO_3, 5 ml of 1 N acetic acid, and from 2.5 to 10 ml of 10^{-3} M reagent. At the same time experiments were carried out with solutions containing the same amount of all the solutions apart from boric acid.

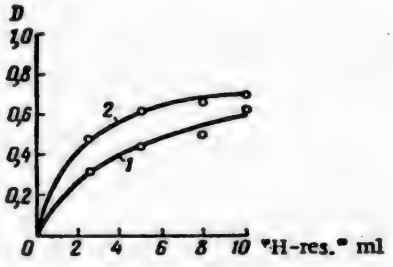


Fig. 2. Relation between the light absorption of solutions containing boric acid, and the amount of reagent.

The light absorption was measured immediately after addition of the reagent, and 24 hours afterwards.

It is evident from the results given in Table 3 that the extinction of the blank even for an amount of reagent equal to 2.5 ml is fairly high (greater than unity) while with increasing amount of reagent, the extinction increases even more. When 5-10 ml of reagent is used, it is so high that the field of vision in the photometer darkens and comparison becomes difficult.

On the other hand, the extinction of solutions containing H_3BO_3 increases with increasing amount of reagent; nevertheless, in the presence of 5-8 ml of reagent, extinction is weak (Fig. 2).

On this basis an amount of reagent less than 5 ml was chosen, for further work; using this amount of reagent – 4 ml – comparison could still be made quite accurately, while this amount of reagent was also sufficient for ensuring complete formation of the H-resorcinol – boric acid complex.

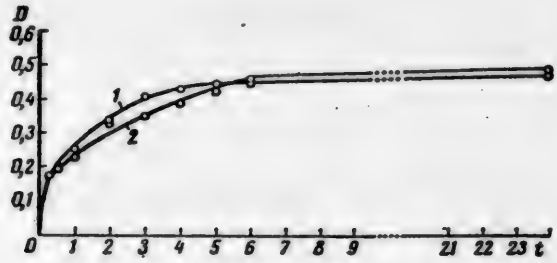


Fig. 3. Relation between color intensity and time of standing of the solution.

In order to establish the length of time for which it is necessary to stand the solution after adding the reagent, for obtaining maximum color intensity, the following experiments were carried out: 2.5 ml of 10^{-3} M H_3BO_3 solution was mixed with 4 ml of 10^{-3} M H-resorcinol and 5 ml of 1 N acetic acid added; the volume was made up to 50 ml. Photometric measurements were made $^1/_4$, $^1/_2$, 1, 2, 3, 4, 5, 6, and 24 hours after mixing the reagents, using the conditions described above.

TABLE 4

Relation Between Light Absorption of the Solution and Amount of Boron

Boron content, in γ	Light absorption of the solution
1.1	0.086
2.2	0.088
5.5	0.151
11.0	0.249
16.5	0.289
22.0	0.366
27.5	0.398
44.0	0.551
66.0	0.634

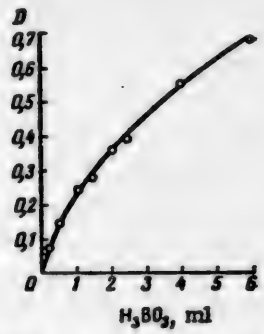


Fig. 4. Relation between the color intensity of the solution and the boron content.

Measurements were carried out both on solutions kept at room temperature, and on solutions which had been heated almost to the boiling point on addition of the reagents and then cooled under tap water.

As the results shown in Fig. 3 demonstrate, the curves already coincide within the course of the first 4-6 hours after addition of reagent, while the further increase in color or light absorption of the solution is insignificant. Accordingly, the colored solution should be allowed to stand for 4-6 hours. Heating of the solution does not seem to be obligatory, since the curves obtained with and without heating coincide.

In order to establish the relation between color intensity and the boron content, a series of solutions were prepared containing from 0.1 to 6.0 ml of 10^{-3} M boron (from 1.1 γ to 66 γ B). 4 ml of reagent was added, followed by 5 ml of 1 N acetic acid, and the volume made up to the mark with water. The light absorption was measured against a blank after 20 hours.

As the results given in Table 4 and Fig. 4 show, the relationship between boron concentration and light absorption is non-linear; consequently, when determining boron by this method it is necessary to construct a calibration curve on the basis of several points.

As a result of all the experiments carried out, the following conditions have been chosen for determining boron by means of H-resorcinol: for amounts of boron from 1.1 γ to 66.0 γ, 4 ml of reagent should be taken (10^{-3} M), together with 5 ml of 1 N acetic acid, and the total volume made up to 50 ml. The color almost reaches its maximum intensity after 4-6 hours and thereafter does not increase appreciably. The relationship between color intensity and boron concentration is curvilinear within these limits.

SUMMARY

The interaction between boric acid and H-resorcinol has been studied. The dissociation constant and the molar extinction coefficient of the compound formed have been determined. The optimum conditions for the photometric determination of boron have been established.

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PHOTOMETRIC DETERMINATION OF GALLIUM BY MEANS OF GALLION

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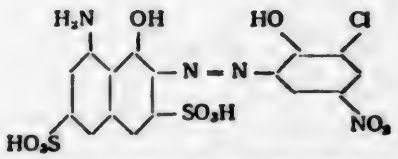
8-Hydroxyquinoline has been used for the photometric determination of gallium [1, 3], as well as quinalizarin [3, 2] which is of low selectivity, and aluminon which shows low sensitivity and forms with gallium, just like quinalizarin, a bright-red colored lake [4]. Recently, rhodamine B [5] has found wide use in the fluorescent determination of gallium. Lukin and Zavarikhina [6] have shown that the product obtained by coupling H-acid with the diazo compound from 2-amino-4-nitro-6-chlorophenol, and arbitrarily called gallion, is an interesting reagent for gallium.



2-hydroxy-3-chloro-5-nitrobenzene-
-(1-azo-2)-1'-hydroxy-8'-alinonaphthalene-
-3',6'-disulfonic acid.

Gallion is a dark-red powder which is soluble in water; a 0.01% transparent aqueous solution has a dark-red color, acid aqueous solutions are bright-red in color [6], while alkaline solutions are violet-blue. The reagent is readily soluble in ethyl and isoamyl alcohols, and also in acetone; it is sparingly soluble in chloroform and dichloroethane. A solution of the reagent forms, at varying pH values, colored compounds with various elements. An aqueous solution of the reagent forms, with gallium, a blue-colored compound.

TABLE 1

Interaction of Metal Ions with Gallion

Element	pH	Color	
		Reagent solution	Compound of element and reagent
Co	4,2—5,6	Rose-violet	Violet
Ni	4,2—5,6	»	Blue-violet
Al	3,2—5,6	»	Blue
Mn	3,4—6,3	»	Violet
Tl	2,0—4,6	»	Blue-violet
Fe^{3+}	2,2—5,6	»	»
Bi	8.5—11	Violet-blue	»
Cr^{III}	9,2—11	»	»
Th	2,4—3,6	Violet-rose	Violet
In	3,2—4,4	Rose-violet	Blue
Ce	2,4—3,8	»	»
Cu	2,2—5,6	»	Violet
Sc	2,2—4,2	»	Blue
Ga	2,2—4,8	»	Pale blue

Gallion changes its color from red to blue-violet in the pH range 3.8-5.8. Above 5.8, the violet-blue color does not change until a pH of 13 is reached. On increasing the pH further, the color starts to change; it first acquires a rose color, and then at pH about 14, the solution has the same color as at pH 4.0 (Fig. 1).

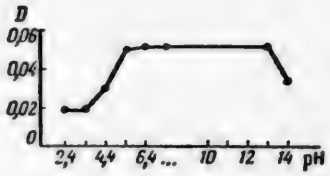


Fig. 1. Change of the color of gallion solutions with pH.

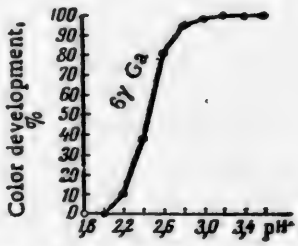


Fig. 2. Intensity of the color of gallion solutions as a function of pH.

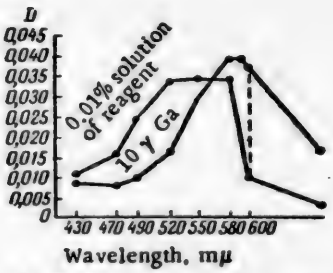


Fig. 3. Determination of the maximum light absorption for the compound formed between gallion and gallium (10 γ of Ga in 10 ml).

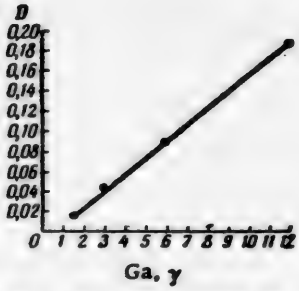


Fig. 4. Relation between optical density and gallium concentration.

The optimum pH range for gallium determination is 2.4-3.4 (Fig. 2). Maximum light absorption is observed at 600 mμ (Fig. 3). For the determination of gallium, it is convenient to use a hydrogen phthalate buffer, although the latter is sensitive to temperature changes, particularly at pH 2.4. When the temperature drops (down to +16°) crystals are deposited.

When optimum conditions are used for determination of gallium (pH of about 3.2), the sensitivity of the reaction amounts to 0.2 γ of Ga in 5 ml of solution.

Conditions used for Gallium Determination. To 2 ml lots of solution containing 0.2, 0.5, 1, 2, 4, 6, 8, and 12 γ of Ga, and 2 ml of water (control) contained in test tubes, was added a hydrogen phthalate buffer with a pH of about 3.2* until the volume was 4.5 ml, when 0.5 ml of a 0.01% aqueous solution of gallion was added. The color developed in the first minute, and was complete in 10-15 minutes. The temperature strongly affects development of the color. Thus, on heating to 60-100°, complete color development is achieved in $1\frac{1}{2}$ - 2 minutes. After cooling, the scale is stable for 40 hours (Table 2). The relationship between color intensity and gallium concentration of the solution is linear (Fig. 4). By heating, it is possible to determine gallium by the method of colorimetric micro-titration. For this purpose, 1 ml of a weakly acid (pH about 2-2.6) or neutral test solution, containing from 0.5 to 12 γ of Ga, was introduced into a test tube, and buffer solution (pH about 3.2) added to bring the volume up to 4.6 ml, 0.4 ml of a 0.01% aqueous solution of gallion was then added. At the same time, into another test tube was introduced 4.6 ml of the same buffer solution and 0.4 ml of gallion solution. Both tubes were immersed in a beaker containing hot water kept constant at about 85°. To the test tube not containing

* The hydrogen phthalate buffer was prepared by mixing 25 ml of a 0.2 M solution of potassium hydrogen phthalate with 7.35 ml of 0.2 M hydrochloric acid and 67.65 ml of water.

the gallium was then added from a buret, carefully, and in small portions, a standard solution of gallium containing 2.5 γ of Ga per ml; towards the end point the solution was added dropwise, until the colors of the test solution and standard solution were the same. Results of such a titration are given in Table 3.

TABLE 2

Stability of the Color of the Gallium Compound at pH about 3.2

Ga taken, in γ	Optical density			
	after 5 min	after 1 hr	after 18 hr	after 40 hr
0,6	0,0018	0,0018	0,0016	0,0016
1,2	0,0027	0,0027	0,0026	0,0026
2,4	0,0052	0,0052	0,0051	0,0052
4,8	0,0109	0,0108	0,0109	0,0109
9,6	0,0230	0,033	0,025	0,0230

TABLE 3

Determination of Gallium by Colorimetric Microtitration.

Ga taken, in γ	Ga found, in γ	Relative error, in %	Ga taken, in γ	Ga found, in γ	Relative error, in %
1,1	1,12	+ 2	7,8	7,85	+0,6
1,7	1,7	0	11,8	11,82	+0,2
2,5	2,52	+0,8	1,50	1,50	0
3,5	3,55	+1,4	2,25	2,25	0
5,2	5,2	+0,9	—	—	—

TABLE 4

Determination of Gallium in the Presence of Other Elements at pH about 3.2.

Gallium intrd. in γ	Gallium found in γ	Error, in γ	Me, in γ	Ratio Ga : Me	Gallium intrd. in γ	Gallium found in γ	Error in γ	Me, in γ	Ratio Ga : Me
0,5	0,5	0	Ge 300	1 : 600	1,0	1,3	+0,3		
2,0	2,0				2,0	2,2	+0,2	In 300	1 : 15
0,5	0,55	±0,05	Pr 100	1 : 200	2,0	2,1	+0,1	Rh 30	1 : 15
2,0	2,1	±0,1			1,0	1,1	+0,1	Tl 1000	1 : 1000
0,5	0,5	0	La 100	1 : 200	1,0	1,0	0	Re 100	1 : 100
2,0	1,8	—0,2			4,0	3,8	—0,2		
0,5	0,5	0	Mn 200	1 : 400	1,0	1,0	0	Pb 100	1 : 100
1,0	1,1	+0,1			2,0	2,0	0		
2,0	1,8	—0,2	Co 100	1 : 200	0,5	0,55	+0,05	Mg 50	1 : 100
0,5	0,55	+0,05			2,0	1,8	—0,2		
4,0	4,0	0	Zn 200	1 : 400	0,5	0,5	0	Ca 100	1 : 200
0,5	0,5	0			1,0	1,0	0	Be 50	1 : 50
0,5	0,4	—0,1	Li 100	1 : 200	1,0	1,0	0	In 50*	1 : 50
1,0	1,1	+0,1			1,0	1,0	0	Al 50*	1 : 50

*Ga was determined in the presence of aluminum and indium at a pH of 2.4.

In Table 4 are given the limiting ratios of gallium to other metals which do not form colored compounds with gallion (Ge, La, Pr, Rh, Te, Tl, Pt, Zn, Hg^{2+}, Ir, Be, Cd, Pb, Ca and Mg), at which gallium can still be

determined with permissible accuracy. Aluminum and indium form colored compounds with gallion at a pH of about 3.2. Nevertheless, in more acid media (pH about 2.4) we were able to determine gallium in the presence of these elements at a ratio of Ga : Al = 1 : 50 and of Ga : In = 1 : 50 (Table 4).

TABLE 5

Determination of Gallium after its Extraction by Isoamyl Alcohol from a Solution Containing Other Elements

Me taken, in γ	Gallium		Relative error, in %
	introduced, in γ	found, in γ	
Al 1000	0.5	0.5	0
Fe^{3+} 250	1.0	0.9	−10
Cu^{2+} 200	1.0	1.0	0
	2.0	1.85	−8
	1.0	1.2	+20
Al 1000	2.0	1.8	−10
Cu 250	2.0	2.25	+12
In 200	2.0	2.15	+7
	1.0	1.15	+15

Fe^{3+} and Cu^{2+} ions strongly interfere with determination of gallium, but at contents of these elements not greater than 50 γ, iron can be reduced by addition of 0.5 ml of a freshly prepared 20% solution of hydroxylamine hydrochloride, while copper can be reduced by addition of 0.25 ml of 0.1 N sodium thiosulfate. After addition of hydroxylamine, excess acid is neutralized with a 2% solution of sodium acetate to a pH of about 2.4-3.2.

TABLE 6

Determination of Gallium after its Extraction with Amyl Acetate from Salts and Minerals*

Natrolite $Na_2(Al_2Si_3O_{10})\cdot 2H_2O$			$K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$			$Al_2(SO_4)_3$			Amazonite $K(AlSi_3O_8)$		
Ga intrd. in γ	Ga found	Relative error, in %	Ga intrd. in γ	Ga found, in γ	Relative error, in %	Ga intrd. in γ	Ga found, in γ	Relative error, in %	Ga intrd. in γ	Ga found in γ	Relative error, in %
—	1,8	—		Not detected	—	—	Not detected	—	—	1,6	—
1,0	2,9	+4	1,0	1,1	10	1,0	1,0	0	2,0	3,8	+5
1,0	2,8	0	1,0	1,0	0	1,0	1,2	+20	2,0	3,5	−3
1,0	3,0	+7	1,0	1,15	+15	1,0	1,1	+10	4,0	5,4	−4
2,0	3,8	0	2,0	1,9	−5	2,0	2,2	+10			
2,0	3,7	−3	2,0	2,2	+10	2,0	2,1	+5			
0,5	2,2	−5									
0,5	2,25	−3									

* Determination was carried out on 5 ml of test solution; total volume 10 ml.

As the results given in Table 4 show, zinc, aluminum, and indium, in small amounts, do not interfere with determination of gallium; large amounts of these elements, however, distort the results for gallium determination. Accordingly, during analysis of aluminosilicates, aluminum alloys, zinc blendes and other materials, where traces of gallium are present, it is necessary to separate the gallium.

Usually, gallium is extracted from interfering elements by extraction with an organic solvent from a hydrochloric acid solution [5, 7]. Use is made of the extraction of gallium by ethyl ether from 6 N hydrochloric acid solution [3]. The ether extracts are evaporated and gallium determined in the residue. Gallium can also be extracted with isopropyl ether [5]. Bearing in mind the high volatility and ready inflammability of ether, we thought it best to extract gallium with isoamyl alcohol and ethyl acetate from a 6 N hydrochloric acid solution. Hydroxylamine

is added to the solution containing gallium and the other elements in order to reduce Fe^{3+}, while thiosulfate is added to reduce Cu^{2+}.

TABLE 7

Determination of Gallium in Minerals and Metallic Aluminum

Sample	Gallium found by means of gallion, in %	Gallium found by means of quinalizarin, in %
Natrolite $Na_2(Al_2Si_3O_{10}) \cdot 2H_2O$	0.018	0.02
Amazonite $K(AlSi_3O_8)$	0.016	0.016
Metallic alluminum	Not detected	Not detected

Procedure for Removal and Determination of Gallium. When the test alloy or mineral is soluble in hydrochloric acid, 0.1 g of sample (weighed out to an accuracy of 0.001 g) is dissolved in 10 ml of hydrochloric acid 1 : 1, and the solution transferred to a separating funnel. The vessel in which the sample is dissolved is carefully washed out with 3 lots of 3 ml of the same hydrochloric acid. To the final solution in the separating funnel is added 3 ml of 20% freshly prepared hydroxylamine hydrochloride solution, 0.25 ml of 0.1 N sodium thiosulfate and (for keeping the acid concentration at 1 : 1) 3.25 ml of concentrated hydrochloric acid (sp. gr. 1.18-1.19). 5-8 ml of amylacetate or isoamyl alcohol is then added and the whole shaken for 1.5-2 minutes, after which the layer of amyl acetate or isoamyl alcohol is transferred to another separating funnel. Extraction is repeated twice again, each time with 5 ml of the organic solvent chosen. The combined extracts are washed three times with hydrochloric acid 1 : 1, containing in each portion of wash liquor 1 ml of 20% hydroxylamine hydrochloride, 0.25 ml of sodium thiosulfate, and 1.25 ml of concentrated hydrochloric acid; washing is carried out with 2-3 ml each time. The washed extract is neutralized in the separating funnel with 2.5% ammonia solution; excess ammonia is added (1-2 ml) and the whole shaken for $1\frac{1}{2}$-2 minutes; the aqueous phase is transferred to a 25-50 ml standard flask. The operation of transferring gallium into the aqueous phase with ammonia is repeated twice again. The aqueous-ammonia layers are added to the same standard flask. The solution in this flask is carefully neutralized with hydrochloric acid 1 : 1, and one drop of acid added in excess. The volume of the solution is made up to the mark with a buffer solution having a pH of about 3.2. Before determining the gallium it is necessary to check the pH of the solution. For this purpose 1-2 ml of the test solution is introduced into a test tube and the volume made up to 5 ml with buffer solution. Into a second test tube is introduced 5 ml of the same buffer solution with an accurately established pH (potentiometrically or otherwise). An equal amount of methyl orange (1-2 drops each) is added to each tube; the color should be the same in both cases. If the test solution should prove to be more acid than it should be, 2% sodium acetate solution is added until the color of the test solution is the same as that of the buffer solution. If, on the other hand, it should prove to be too alkaline, then 0.1 N hydrochloric acid is added. The amount of sodium acetate or 0.1 N hydrochloric acid established is only added to the test solution. The scale is prepared over the range 0.5-12 γ Ga; buffer solution (pH about 3.2) is then added to bring the volume up to 4.5 ml, and 0.5 ml of a 0.01% aqueous solution of gallion added to each. The test solution and the series of standard solutions forming the scale, contained in test tubes, are immersed in a vessel with boiling water for 1.5-2 minutes, and then cooled and the colors compared.

In those cases where the mineral does not dissolve in hydrochloric acid, it is fused and the melt dissolved in HCl.

Using the conditions described, gallium was determined in synthetic mixtures, and also in metallic aluminum, aluminum-potassium alum, in aluminum salts and in the minerals natrolite and amazonite. The results obtained are given in Tables 5-7.

SUMMARY

The product formed by coupling H-acid with the diazo compound from 2-amino-4-nitro-6-chlorophenol

reacts with gallium to form a colored compound at a pH of 2.4-3.2 which is stable for 40 hours. The sensitivity of the reaction is 0.2 γ of Ga in 5 ml of solution.

A method is described for the determination of gallium in various test materials.

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*Original Russian pagination. See C. B. Translation.

DETERMINATION OF INDIUM PRESENT AS AN IMPURITY IN GERMANIUM

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The photometric methods which are known for the determination of indium – those based on 8-hydroxyquinoline or morine – are not specific enough. In the presence of various masking agents, added in order to enhance the specificity, the sensitivity of these methods decreases appreciably. A method described recently for the determination of indium as an impurity in germanium by means of 8-hydroxyquinoline [1], permits determination of indium down to $1 \cdot 10^{-4}$%, but this is not always low enough.

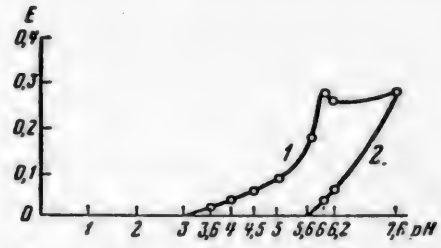

Fig. 1. Effect of pH on color development: 1) Indium complex; 2) reagent.

With the aim of finding a more sensitive, and reasonably specific method for determining indium as as impurity in germanium, we tested various color reactions for the former. Of the color reactions tested, the one that proved most convenient for quantitative determination was the reaction with diphenylcarbazone described by Poluektov and N. K. Kiseleva [2].

Diphenylcarbazone as a Reagent for Indium. Diphenylcarbazone in a very weakly acid medium (pH < 7) gives a violet color with indium; when large amounts of indium are present, a violet precipitate is formed. When no indium is present the solution remains a brownish-yellow color. The relation between the color intensity and pH of the solution is shown in Fig. 1.

Tests were carried out as follows: to 1 ml of a neutral solution of indium chloride (5 γ of In) were added 0.5 ml of a 0.1% solution of diphenylcarbazone and 4 ml of an appropriate buffer solution. The optical density was measured 5 minutes afterwards on a Pulfrich photometer using a 10 mm cell; the wave-length used was 570 mμ while water served as the reference solution. A blank was carried out under the same conditions, indium being omitted. It is evident, from the Fig. that the optimum pH of the solution is 6 (hydrogen phthalate buffer).

At pH 5-6, 50 γ of each of the following elements does not react with diphenylcarbazone: magnesium, calcium, aluminum, chromium, (III), tin (IV), antimony, arsenic, silver, germanium, and thallium. Copper (II) and zinc behave like indium. Gallium also reacts, but the reaction sensitivity is considerably less in this case than for indium. Iron (III) exhibits a characteristic behavior; while it does not itself react with diphenylcarbazone under the conditions used, it almost completely masks indium, presumably as the result of trapping of indium by the precipitate of ferric hydroxide formed during hydrolysis at the high pH of the solution. Even as little as 2 γ of iron halves the color intensity resulting from 5 γ of indium.

It was found possible to eliminate interference from iron by using thiourea; nevertheless this could only be done at pH 5.6 (hydrochloric-pyridine buffer). No method of masking iron could be devised when the pH was 6 (hydrogen phthalate buffer). The use of a reducing agent (ascorbic acid, thioglycollic acid) for converting iron into the divalent state was not possible in this instance because of the reduction of diphenylcarbazone to carbazide, which does not react with indium. Other complexing agents hydroxycarboxylic acids, cyanide) mask indium as well as iron. In the presence of acetylacetone, iron fluoride reacts with diphenylcarbazone.

Thiourea, in addition to masking iron, also masks copper and weakens the reaction with zinc.

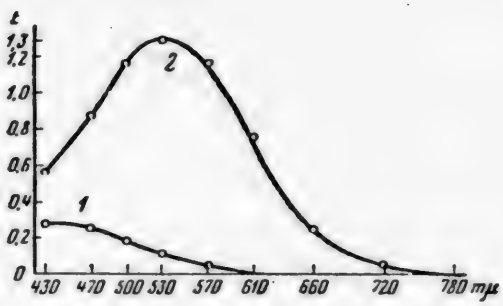

Fig. 2. Absorption curves: 1) Reagent; 2) reagent + indium.

Because of the necessity of eliminating interference from iron, it was found best to determine indium at a pH of 5.6. At this pH the color intensity, as is evident from Fig. 1, is half of that at pH 6; nevertheless the reaction gains in specificity.

Absorption curves for the reagent itself and for the indium-reagent complex are shown in Fig. 2. The solutions used were prepared as indicated above, but the indium was taken in excess with respect to the reagent (25 γ). The buffer was a hydrochloric-pyridine mixture with a pH of 5.6. It follows from Fig. 2 that the absorption maximum of the indium complex lies at 530 mμ; at this wave-length, however, absorption by the reagent itself is discernible. It is more convenient, therefore, to determine indium at 570 mμ, where the reagent itself does not absorb, while the absorption exhibited by the complex is only slightly less than the maximum absorption.

Within the limits 0.4-5 γ, solutions of indium conform to the Beer law (Fig. 3).

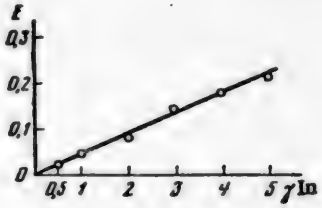

Fig. 3. Relation between color intensity and amount of indium.

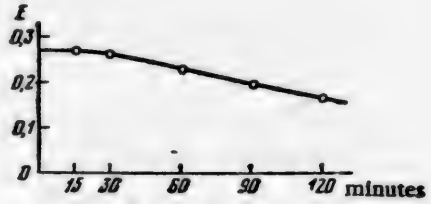

Fig. 4. Effect of time on color development.

In these experiments, thiourea (0.5 ml of a 10% solution) was added to the reaction solutions. The buffer was a hydrochloric–pyridine mixture with a pH of 5.6. Optical density was measured in a Pulfrich photometer at 570 mμ. Measurements can also be made on a FEK-M photocolorimeter, but in this case it is necessary to use a combined filter (green and orange glass).

It can be seen from Fig. 4 that the color is stable for less than 15 minutes; at the end of this time it gradually weakens, mainly because of coagulation of the complex. Accordingly, all measurements should be carried out not later than 10 minutes after preparing the solutions.

Determination of Indium in Germanium. Determination of micro amounts of indium in germanium is possible after removal of germanium by distillation in the form of its tetrachloride. All the indium remains in the residue; this fact was checked by means of the radioisotope In^{114}.

During the analysis of pure germanium dioxide, using purified reagents, the indium can be determined directly in the residue after removal of germanium. When, however, impure germanium dioxide is analyzed, or metallic germanium, the residue may contain interfering metals, mainly iron. In such cases, it is necessary to separate the indium; this is readily carried out by extraction from hydrobromic acid with ether. In order to prevent iron from passing into the extract at the same time, extraction is carried out in the presence of titanium trichloride.

The use of a hydrochloric–pyridine buffer, which has a comparatively low capacity for the determination of indium, demands that the test solution be neutralized as far as possible. During evaporation of acid solutions to dryness, hydrolysis of indium salts is observed and this can lead to low results. Addition of a small amount of sodium chloride to the indium solution prior to evaporation prevents hydrolysis, because of the formation of sodium chloroindiate. Sodium chloride does not subsequently interfere with indium determination.

Reagents. Concentrated hydrochloric acid. This is obtained by saturating twice-distilled water with hydrogen chloride in a quartz vessel.

2. Nitric acid, concentrated, purified by distillation in a quartz apparatus.

3. Hydrobromic acid, 5 N, saturated with ether. The commercial acid is purified by distillation in a quartz apparatus and diluted with water to the requisite concentration. This 5 N solution is saturated with ether by shaking it in a separating funnel with an equal volume of ether free from peroxides, and, after separating into two layers, keeping the two phases separately.

4. Peroxide-free diethyl ether. The ether is purified by distillation after standing over sodium metal. The distilled ether is saturated with hydrobromic acid.

5. Sodium chloride, 1% solution.

6. Titanium trichloride, 20% solution in 6 N hydrochloric acid.

7. Thiourea, 10% solution.

8. Pyridine buffer. To 98 ml of 0.01 N hydrochloric acid is added 2 ml of a 10% solution of pyridine. The pyridine is purified by distillation over sodium hydroxide.

9. Diphenylcarbazone, 0.1% solution in 96% ethanol.

TABLE 1

Determination of Indium in the Absence of Germanium. Complete Analysis

In taken, in γ	In found, in γ	Difference, in γ
0.5	0.5	−0.1
1.0	1.1	+0.1
2.0	2.0	0
4.0	4.0	0
5.0	4.9	−0.1

Calibration Curve. Into quartz crucibles is measured standard indium solution (5 γ per ml) in amounts corresponding to 0.5, 1, 2, 3, 4, and 5 γ of In; one crucible is left empty (for the blank). Water is added to each crucible to bring the volume up to 1 ml; 0.2 ml of sodium chloride and 0.5 ml of hydrochloric acid is then added to each crucible; the contents of each crucible is then treated as follows. It is evaporated to dryness on a water bath and the residue moistened with 1 ml of water; the water is used for washing down the sides of the crucible, after which it is evaporated to dryness again. The dry residue is transferred to a test tube using 1.5 ml of water; 0.5 ml of thiourea solution, 0.5 ml of diphenylcarbazone and 2.5 ml of the pyridine buffer are added to each; the liquid is mixed after addition of each reagent. After 5 minutes the optical density of the solution is measured using a 10 mm cell against the blank solution; the wave length used is 570 mμ; measurements can be made either on a photometer, or on a photocolorimeter with a double filter (green and orange). A calibration curve is constructed on the basis of the results obtained.

TABLE 2

Determination of Indium added to 2 g of GeO_2, without Ether Extraction

In added		In found		Difference	
in γ	in % × 10^5	in γ	in % × 10^5	in γ	in % × 10^5
0	0	0	0	—	—
0,5	2,5	0,47	2,4	−0,03	−0,1
1	5	1	5	0	0
1	5	1,1	5,5	+0,1	+0,5
3	15	3,1	15,5	+0,1	+0,5
3	15	2,9	14,5	−0,1	−0,5
4	20	3,8	19	−0,2	−1

TABLE 3

Determination of Indium added to Metallic Germanium; (complete analysis)

Weight of Ge, in g	In added		In found		Difference	
	in γ	in % × 10^5	in γ	in % × 10^5	in γ	in % × 10^5
2	0	0	0	0	—	—
2	0,5	2,5	0,5	2,5	0	0
2	1	5	0,8	4	−0,2	−1
1	1	10	1	10	0	0
1	3	30	3	30	0	0
1	4	40	3,8	38	−0,2	−2
1	5	50	5	50	0	0

Determination of Indium. 1-2 g of coarse germanium powder is carefully heated in a quartz flask with

10 ml of 12 N hydrochloric acid and 2 ml of nitric acid; the heating, which is carried out on a sand bath, is continued until the volume is 2-3 ml. 10 ml of hydrochloric acid and 2 ml of nitric acid are added again, and the whole heated until all the metal particles have dissolved. Where necessary, the residue should be given a thrid treatment with addition of acid. The acids are finally evaporated until a residue of about 1 ml remains.

During the analysis of germanium dioxide, 2 g of sample is placed in a quartz flask and 20 ml of 8 N hydrochloric acid added; the mixture is evaporated until a volume of about 1 ml remains in the flask. Germanium may be separated from the collected distillates.

After dissolution, and removal of germanium by distillation, the residue in the flask is washed into a quartz crucible with the aid of 5 ml of water; 0.2 ml of sodium chloride solution is added and the mixture evaporated to dryness on a water bath. The residue is dissolved in 5 ml of hydrobromic acid and transferred to a separating funnel, 0.1 ml of titranium trichloride is added, and the solution extracted three times with 3 ml lots of ether. Shaking is carried out for one minute each time. The combined extracts are washed 3 times with 3 ml lots of hydrobromic acid. The washed extracts are poured into a quartz crucible, and 0.2 ml of sodium chloride solution and 0.5 ml of 6 N hydrochloric acid added; the mixture is then evaporated to dryness, first on a warm bath, and finally on a boiling water bath. The residue is moistened with water, the water being added so as to wash down the walls, and the whole evaporated to dryness once again. The residue is finally washed into a test tube by means of 1.5 ml of water. The procedure subsequently followed is the same as that described for construction of a calibration curve. Measurements are made against a blank solution (the same solution, but without indium).

Compact germanium is ground up in an agate mortar between layers of white cotton fabric. Compact germanium can also be brought into solution by anode dissolution [3].

As the results given in Tables 1-3 show, the method gives satisfactory results. When 2 g of germanium or its dioxide is taken for analysis, it is possible to determine as little as 0.4 γ of In; this corresponds to $2 \cdot 10^{-5}$%. From the point of view of simplicity and specificity, the method is applicable to the analysis of germanium for its indium content, with the sensitivity indicated.

SUMMARY

A method for the photometric determination of indium, based on the use of diphenylcarbazone, has been developed. The method permits determination of 0.4 γ of In in 5 ml of solution. The method is applicable to the determination of indium present as impurity in metallic germanium and germanium dioxide; the sensitivity is $2 \cdot 10^{-5}$%.

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*Original Russian pagination. See C. B. Translation.

**In Russian.

APPLICATION OF THE METHOD OF ADDITIONS DURING TITRIMETRIC DETERMINATION OF BISMUTH

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Of the known titrimetric methods of determining bismuth [1] the most promising would appear to be the phosphate method, although, without exception, all the variants of the titrimetric method hitherto suggested possess poor reproducibility and are not accurate enough. The hardly appreciable solubility of the precipitate of $BiPO_4$ in dilute nitric acid, the rapid formation of a heavy crystalline precipitate, etc., however, do open up prospects of using the formation of $BiPO_4$ as a method for the titrimetric determination of Bi. The reason for the lack of success hitherto can be attributed to the absence of satisfactory indicators for clearly establishing the equivalence point.

The method consists of precipitating bismuth from nitric acid solution in the presence of sodium acetate, using excess of a standard solution of sodium phosphate. After filtering off and washing the precipitated $BiPO_4$, the excess sodium phosphate is titrated with standard uranyl acetate. The equivalence point is established by an external indicator—potassium ferrocyanide. Other research workers [2] have titrated the excess phosphoric acid with uranyl acetate, and determined the equivalence point with an external indicator (tincture of cochineal). A method even more complicated [3] is addition of excess standard Na_2HPO_4 solution to a boiling sample of the bismuth nitrate solution. The $BiPO_4$ precipitate formed is then filtered off and washed, and the filtrate plus washings transferred to a standard flask in which it is neutralized with sodium hydroxide; 50 ml of 0.1 N sodium acetate is then added followed by 50 ml of standard $AgNO_3$ and the volume of the solution made up to 500 ml. An aliquot of this solution plus excess $AgNO_3$ is finally titrated by the Volhard method. This method, as a consequence of the numerous operations involved, which lead to appreciable losses, does not give reliable results.

TABLE 1

Determination of Bismuth by the Ehrenfeld, Krause, and Addition Methods Respectively

Bi taken, in g	Bi found					
	Ehrenfeld method		Krause method		Addition method	
	in g	Error, in %	in g	Error, in %	in g	Error, in %
0,050	0,046	−8,0	0,048	−4,0	0,0505	+1,0
0,050	0,047	−6,0	0,052	+4,0	0,0500	+0,0
0,080	0,075	−6,3	0,076	−5,0	0,0805	±0,63
0,080	0,085	+6,3	0,083	+3,7	0,798	−0,25
0,120	0,125	+4,2	0,124	+3,3	0,121	+0,83
0,120	0,115	−4,2	0,115	−4,2	0,120	±0,0
0,160	0,170	+6,3	0,165	+3,1	0,1615	±0,94
0,160	0,155	−3,2	0,153	−4,4	0,1610	+0,63

A simpler method [4] involving direct titration with standard Na_2HPO_4 neutralized with ammonia, of the bismuth solution acidified with a few drops of nitric acid, does not give any better results. The equivalence point

is established by the change in color of haematin indicator paper. In our experiments the experimental error of this method varied from + 7.0 to + 9.0% during determination of from 0.04 to 0.1 g of Bi.

The method of additions, which is applicable in this case, gave satisfactory results (Table 1).

TABLE 2

Dependence of the Degree of Oxidation of Metallic Bismuth (0.178 g) on the Concentration of $FeCl_3$

$FeCl_3$ solution added, in ml	Amount of Fe^{3+} participating in the reaction, in g/ion	By the usual method			By the addition method		
		$KMnO_4$ solution used, in ml	Bi found, in g	Error, in %	$KMnO_4$ solution used, in ml	Bi found, in g	Error, in %
8.0	0.248	21.2	0.162	−8.7	22.10	0.1690	−5.0
10.0	0.356	22.1	0.169	−5.0	22.80	0.1755	−1.4
12.0	0.427	22.4	0.172	−3.4	22.83	0.1760	−1.1
15.0	0.533	22.7	0.174	−2.0	23.0	0.1770	−0.6

Of the methods based on preliminary reduction of bismuth ions to the metallic state by means of magnesium, zinc, copper [5], aluminum [6], and other metals, with subsequent oxidation of bismuth metal with ferric chloride, the most simple, rapid, and accurate method is the one involving reduction with aluminum dust.

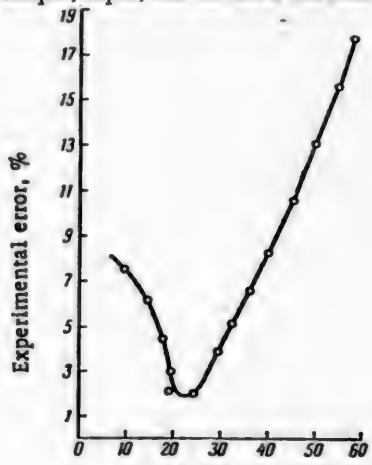

Fig. 1. Relationship between the accuracy of titration of ferric chloride solution and the amount of Reinhardt-Zimmerman mixture.

We have studied the kinetics of the reduction of bismuth, and the effect of ferric chloride concentration on the oxidation of bismuth metals, and have established the optimum amounts of the Reinhardt-Zimmerman mixture that should be added.

For the determination of bismuth a weakly acid solution containing up to 0.25 g of bismuth was mixed with 0.1 g of freshly prepared aluminum dust or copper turnings, and the mixture allowed to react for 15 minutes after addition of the reagents and shaking. 40 ml of 5% potassium hydroxide was added and the whole boiled until all the aluminum had dissolved; the mixture was then diluted with distilled water and the precipitate decanted through a filter; the spongy, metallic deposit of bismuth was filtered and washed with warm distilled water, and treated with 15 ml of ferric chloride solution (200 g of $FeCl_3$, 250 ml of concentrated HCl, and the volume made up to 1 liter with distilled water). To this mixture was added the Reinhardt-Zimmerman mixture; the whole was then greatly diluted, and the ferrous ions formed as the result of oxidation of metallic bismuth titrated with 0.1 N $KMnO_4$.

The relationship between the degree of oxidation of metallic bismuth and the amount of $FeCl_3$ is shown in Table 2.

During titration of $FeCl_3$ solution with permanganate, Reinhardt-Zimmerman (20 ml) was added to the solution being titrated. During oxidation of 0.25 g of Bi, the optimum amount of $FeCl_3$ used should amount to not less than three equivalents per equivalent of bismuth. On increasing the amount of $FeCl_3$ beyond this amount, the experimental error increases rapidly. Even under optimum conditions, however, when the usual method is used, the experimental error is high; it amounts to 2 to 3%. When the method of additions is used, the error drops to 1.4 to 0.6%.

During titration of divalent iron with permanganate in the presence of chloride ions, induced oxidation of Cl^- occurs. In order to prevent oxidation of chloride ions, various amounts of Reinhardt-Zimmerman mixture are added to the liquid being titrated. When this technique has been used previously, various authors have obtained conflicting results. We studied the effect of the amount of this mixture on the accuracy and reproducibility of $FeCl_2$ determination, and established (Fig. 1) that the best results are obtained when 20-25 ml of this mixture is taken per 10 ml of iron chloride solution. On decreasing or increasing this amount of the mixture, the error increases sharply.

Rupp [6] established that Fe^{2+} in the presence of excess phosphoric acid is oxidized very slowly, presumably as the result of the formation of fairly stable ferrous–phosphate complexes [7-9] of the type $H_4[Fe(PO_4)_2]$ and $H_7[Fe(PO_4)_3]$ etc. Accordingly, on addition of large amounts of Reinhardt-Zimmerman mixture, titration of iron gives a considerable negative error.

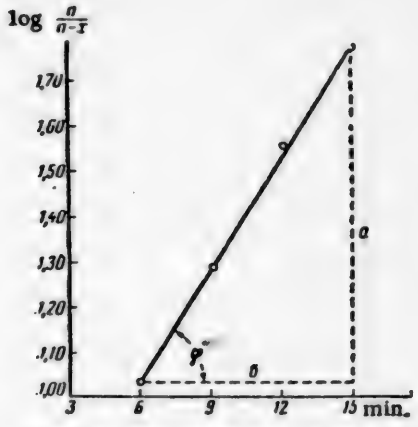

Fig. 2. Kinetics of the reduction of bismuth by metallic aluminum: a) Initial bismuth concentration; a - x) its concentration after time t.

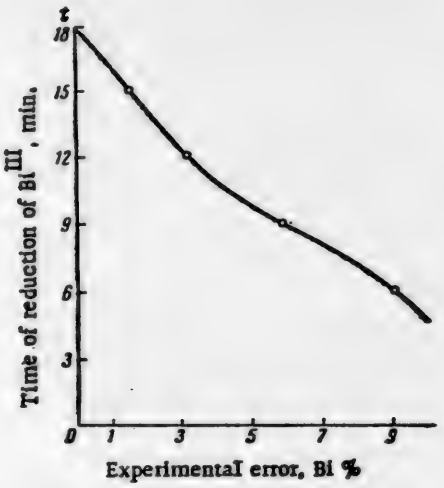

Fig. 3. Experimental error in the determination of bismuth as a function of the duration of reduction with metallic aluminum.

Results of a study of the kinetics of the reduction of bismuth by metallic aluminum at 40° are given in Fig. 2. In this case, a function of the formula given below is observed.

$$K = \frac{1}{t} \lg \frac{a}{a-x}.$$

K = 0.125 at 40°. Bismuth is reduced almost completely after 18 minutes (Fig. 3).

SUMMARY

1. It has been shown that the method of additions, when applied to the titrimetric determination of bismuth, leads to increased accuracy and reproducibility of the results.

2. The best titrimetric method of determining bismuth is the one involving its preliminary reduction with metallic aluminum followed by oxidation of the reduced bismuth with excess ferric chloride.

3. The optimum conditions have been established for oxidation of metallic bismtuh with ferric chloride solution.

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ORGANIC COPRECIPITANTS

COMMUNICATION 9. CONCENTRATION AND SPECTROGRAPHIC DETERMINATION OF MOLYBDENUM IN NATURAL WATERS*

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The presence of molybdenum in natural waters can serve as a prospecting sign for molybdenum, tungsten, and also certain types of copper and cobalt deposits. In natural waters which are found outside the influence of ore deposits, and which have a mineral content of up to 1-2 g/liter, the molybdenum content, usually, does not exceed 10^{-7}-10^{-6} g/liter. Near ore bodies containing molybdenum, the molybdenum content may increase to 10^{-4}-10^{-3} g/liter, for waters with the mineral content indicated above [1]. For the determination of molybdenum at this concentration in natural waters it is necessary to use highly sensitive methods, the most important of which is the spectrographic method.

Nevertheless, the amount of molybdenum and other micro elements in natural water is usually below the sensitivity of the spectrographic method; accordingly spectrographic determination of micro elements in water should be preceded by preliminary concentration of the test elements.

Concentration of the elements can be effected either by evaporating the water to give a dry residue, or by using such techniques as extraction and coprecipitation with inorganic or organic coprecipitants.

The published methods for the quantitative determination of molybdenum in natural waters [2-5] recommend preliminary concentration of molybdenum followed by photometeric determination.

Spectrographic determination of molybdenum in the dry residues from natural waters has been described previously [6]. This method permits determination of $2 \cdot 10^{-4}$ % of molybdenum in the dry residues with a probable error of ± 10%, and, consequently, for a mineral content of 0.1 g/liter, determination of 0.2 γ of molybdenum in 1 liter of water. The essential drawback of this method is the rapid decrease in sensitivity with increasing mineral content of the water. Thus, the method is no longer fully applicable to water containing 5-10 g/liter of minerals. The way out of the dilemma is preliminary concentration of molybdenum.

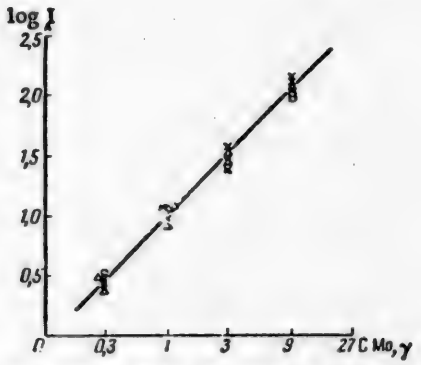
Molybdenum can conveniently be concentrated by coprecipitating it with methyl violet tannate [7]. In a medium of 0.2 N hydrochloric acid, where quantitative coprecipitation of molybdenum occurs, such elements as calcium, magensium, sodium, potassium and others which constitute the major part of the mineral component, are not trapped by methyl violet tannate.

Concentration of molybdenum with organic coprecipitants, at the same time, eliminates the interference of the mineral content of the water with its spectrographic determination.

The study of the applicability of the method of concentrating molybdenum with precipitated methyl violet tannate was carried out with the aid of synthetic waters, corresponding approximately in their cation composition to natural waters, and also on natural water free from molybdenum; for this purpose, 200 ml of such water was acidified until the solution was 0.2 N with respect to HCl. Sodium molybdate solution containing 0.3-27 γ of

* Communication 8, J. Anal. Chem. 13, 79 (1958). [See English Translation].

molybdenum was then added; the liquids were finally mixed and precipitation carried out. The molybdenum content of the precipitate was determined spectrographically by evaporating a sample in the carbon electrode of an a.c. arc, with subsequent measurement of the absolute intensity of the most sensitive molybdenum line Mo 1R--3132.6 A, taking into account the near background.



Relation between the intensity of the line Mo - 1 - R = 3132.6 A and the molybdenum content of the sample, after concentration of the molybdenum by coprecipitation with methyl violet tannate from synthetic and natural waters with varying mineral contents:

- • – Water with high mineral contents;
- o – Water with average mineral contents;
- Δ – Water with low mineral contents;
- × – Twice-distilled water.

Calibration curves were constructed (Fig. 1) by using standard powders which were photographed on the same photographic plate as the test samples. Standard powders containing 0.3, 1, 3, 9 and 27 γ of molybdenum were prepared by coprecipitating molybdenum from twice-distilled water by the method described.

Results of experiments given in Table 1 and in Fig. 1 show that preliminary concentration of molybdenum by coprecipitation with methyl violet tannate is suitable for water with varying mineral content. The mean probable error of the method is ± 12%.

Results for the determination of the molybdenum content of natural waters are given in Table 2.

The Method Used for Concentrating Molybdenum from Natural Waters

Reagents Required:

1) 2% aqueous solution of methyl violet; 2) 2% aqueous solution of tannin – this should not be kept for more than 2-3 days; 3) hydrochloric acid, about 6 N, distilled in a quartz apparatus; 4) water, twice distilled in an apparatus with a quartz condenser; 5) wash solution: to 1000 ml of water is added 20 ml of hydrochloric acid, 0.5 ml of tannin solution and 2 ml of methyl violet solution; 6) standard molybdenum solution, used for constructing the calibration curve.

a) Stock solution: 15 mg of MoO_3 is dissolved in 15-20 ml of about 0.5 N NaOH, and the solution diluted to 50 ml with water, it is then acidified with 3.5 ml of 6 N HCl and made up to the mark with water; the final solution contains 100 γ/ml of Mo; b) working solution: 1 ml of the stock solution is diluted with water to 100 ml; this solution contains 1 γ/ml of Mo.

TABLE 1

Spectrographic Determination of Molybdenum in Natural and Synthetic Waters with Varying Mineral Contents, after Coprecipitation of Molybdenum with Methyl Violet Tannate. Molybdenum could not be detected in the orginal waters.

Molybdenum, in γ		Error, in %	Molybdenum, in γ		Error, in %	Molybdenum, in γ		Error, in %	Molybdenum, in γ		Error, in %
added	found		added	found		added	found		added	found	
—	0	—	1,0	0,97	—3,0	3,0	2,3	—23	9,0	8,0	—11
0,3	0,25	18	1,0	1,2	+20	3,0	2,8	-6,6	9,0	8,8	—2,2
0,3	0,28	—6,6	1,0	1,2	+20	3,0	2,8	—6,6	9,0	8,9	—1,1
0,3	0,31	+1,6	1,0	1,2	+20	3,0	2,9	—3,3	9,0	9,1	+1,1
0,3	0,33	+10	1,0	0,96	—4,0	3,0	3,0	0	9,0	10,2	+13
0,3	0,36	+18	1,0	1,1	+10	3,0	3,3	+10	9,0	10,6	+18
1,0	0,62	—38	1,0	1,2	+20	3,0	2,8	6,6	9,0	9,0	0
1,0	0,64	—36	3,0	2,3	—23	3,0	3,6	+20	27	30	+11
1,0	0,88	—12				9,0	7,8	+24			

Mean probable error ± 12%.

All the reagents used as well as the ashless filter paper must be checked spectrographically for their molybdenum contents.

Since normal glass may contain molybdenum, coprecipitation should be effected in a quartz vessel.

TABLE 2

Comparative Spectrographic and Photometeric Determination of Molybdenum in Natural Waters

Direct, semi--quantitative spectrographic determination of the dry residues	Quantitative spectrographic determination after concentration of the molybdenum by the recommended method, in γ/l	Photometric determination,* in γ/l	Direct, semi--quantitative spectrographic determination of the dry residues	Quantitative spectrographic determination after concentration of the molybdenum by the recommended method in γ/l	Photometric determination,* in γ/l
Insignificant traces	2.9	1.6	Insignificant traces	2.1	
"	0.8	0.8	"	24.5	0.8
"	0.7	0.8	Traces	6.8	16
Not detected	14.5	14.0	"	12.0	4.8
Insignificant traces	1.85	Traces	Not detected		10.0
Traces	1.3	1.0	Traces	7.8	3.0
			"	10.0	5.0

* Photometric determination of molybdenum was carried out in the chemical laboratory of the All--Union Scientific Research Institute of Hydrogeology and Engineering Geology (VSEGINGEO) by the method described in [3].

Coprecipitation of Molybdenum. To about 1 liter of natural water filtered if necessary – is added 30 ml of hydrochloric acid followed by 2.5 ml of tannin solution per 100 ml of the water and, dropwise with stirring, 5 ml of methyl violet solution per 100 ml of water. Solution plus precipitate are allowed to stand for 30-40 minutes, after which the precipitate is filtered through a paper filter moistened with wash solution. The first portions of the filtrate are retured for a second filtration. The precipitate is washed 3-4 times with wash solution, and then transferred together with the filter paper to a quartz crucible.

Before ashing, 30, mg of a "base" containing a mixture of equal parts by weight of anhydrous Na_2SO_4, $CaSO_4$, and $MgSO_4$ is placed on the precipitate. This is effected as follows: 1-2 ml of water is added to 30 mg of the mixture mentioned contained in a small beaker; the mixture is brought into suspension and then by means of a capillary, this suspension is poured over all the precipitate. The beaker is rinsed out with 1 ml of water and this also transferred onto the precipitate. The filter paper placed in the crucible is wrapped up by means of a glass rod and moistened with 5-7 drops of sulfuric acid (1 : 1); it is then dried under a drying lamp and ashed in a muffle at a temperature not higher than 500°. The molybdenum is determined in the residue spectrographically.

Spectrographic Determination of Molybdenum in the Concentrates Obtained. Test waters and portions of twice-distilled water to which had been added known amounts of molybdenum were concentrated by the method described. After addition of "base" to all the concentrates, and after ashing, and triturating with alcohol, a residue is obtained from which 15 mg aliquots are weighed out. These portions are placed in the crater of the lower carbon electrodes having an external diameter of 5 mm and inner diameter of 3.5 mm, and a depth of 4 mm. The upper electrode is sharpened to a cone with an area of 1 mm.

Evaporation of the aliquot is carried out in an ac carbon arc arranged vertically; the arc is fed from a 220 volt supply.

A DG-1 arc generator is used. The discharge gap in the firing circuit of the arc is 0.45 mm. The current

strength is 16-18 amp. The interelectrode distance is 2 mm. The intermediate diaphragm is equal to 0.5; using this diaphragm it is possible to get normally exposed spectra and to control the distance between the electrodes.

The spectra are photographed in an ISP-22 quartz spectrograph with a three-lens illuminating system, at a slit width for the spectrograph of 0.01 mm.

The plates used are "Spectrographic Type II" with a sensitivity of 32° GOST.

Development is carried out at 18° for a period of 4 minutes in a standard methol–hydroquinone developer.

The blackening of the analytical lines in the molybdenum spectrum is measured on a MF-2 microphotometer.

On the basis of the characteristic curve of the photographic plate, and by means of calculating tables, blackening of the lines in the molybdenum spectrum is converted to line intensity, taking into account the effect of the background.

The sensitivity and accuracy of the method developed for the quantitative determination of molybdenum satisfy the requirements of hydrochemical methods of prospecting for ore deposits.

SUMMARY

1. Precipitated methyl violet, deposited from 0.2 N hydrochloric acid, quantitatively traps molybdenum present in solution; this fact can be used for concentrating the molybdenum with a view to its subsequent spectrographic determination.

2. To each 100 ml of solution, with an acidity of 0.2 N with respect to HCl, is added 5 ml of 2% methyl violet solution and 2.5 ml of 2% tannin solution. The precipitate is filtered, and washed, and, after adding 30 mg of "base," ashed at a temperature not higher than 500°. Molybdenum is determined spectrographically in the residue.

3. It has been shown that by using an a.c. carbon arc as the source of spectrum excitation, and by measuring the absolute intensity of the molybdenum line Mo 1R-3121.6 A, it is possible to determine 0.3-27 γ Mo with a probable error of ± 12%.

4. The technique permits determination of 0.3 γ of molybdenum in 1 liter of water with any mineral content.

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* In Russian.

THE EFFECT OF QUADRIVALENT VANADIUM ON THE REDUCTION OF URANIUM ON A DROPPING MERCURY ELECTRODE

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The polarographic method has been widely used for the determination of small amounts of uranium. The behavior of uranium in all its oxidation states on the dropping mercury electrode has been studied fairly thoroughly; the nature and mechanism of the electrode reactions of uranium have not generated any doubts.

Uranyl salts in weakly acid solutions give two polarographic waves with half-wave potentials at −0.19 volt and −0.92 volt relative to the saturated calomel electrode; the first of them corresponds to the reversible reduction of uranyl ions to quinquevalent uranium ions, while the second corresponds to the two successive stages in the further reduction of quinquevalent uranium to quadrivalent and trivalent uranium [1-4]. Uranium is usually determined polarographically on the basis of the first wave, the height of which, in neutral or weakly acid solutions, is proportional to uranium concentration [1, 5-7]. Nevertheless, the presence of vanadium both quinquevalent and quadrivalent, complicates the polarographic determination of uranium, by increasing the limiting current and leading to the formation of an additional wave at approximately −0.5 volt (with respect to the saturated calomel electrode) which is not present on the polarograms of uranium on its own, or of those of quinquevalent and quadrivalent vanadium. There are references in the literature to the interfering action of vanadium during the polarographic determination of uranium [6], but the reason for this interference is still unknown. Vinogradov [8] has indicated that it should be possible to determine uranium polarographically in the presence of vanadium by using lactic acid as a supporting electrolyte.

The work was carried out on the SGM-8 polarograph made by the "Geologorazvedka" factory; the maximum sensitivity of the galvanometer was $3 \cdot 10^{-9}$ a/mm/m. The constant of the dropping electrode was $m^{2/3} \tau^{1/6} = 2.28\ mg^{2/3}\ sec^{-1/2}$. Experiments were carried out in an air thermostat fitted with a bimetallic thermoregulator, the temperature being controlled at 20.0 ± 0.2°. The reference electrode was a saturated calomel electrode. All the values of the half-wave potentials quoted in this article are given relative to the saturated calomel electrode.

The solutions were prepared in twice-distilled water. The stock solution of sexivalent uranium was prepared by dissolving uranyl sulfate in water; the uranium content of this solution was established both gravimetrically and titrimetrically. The stock solution of quadrivalent vanadium was prepared by dissolving purified ammonium metavanadate in water and subsequently reducing it with sulfur dioxide. The vanadium concentration was determined titrimetrically. Trivalent vanadium was obtained by reducing the solution of quadrivalent vanadium on a mercury cathode.

The supporting electrolyte was 0.1 N potassium chloride containing 0.55 g-equivalents/liter of hydrochloric acid.

Analysis of Some of the Polarographic Waves of Uranium and Vanadium. In order to study the nature of the polarographic waves of uranium and quadrivalent vanadium, a graphical analysis was made of the waves obtained in 0.1 N KCl and 0.05 N HCl, using the well-known equations for polarographic waves.

$$\varphi = \varphi_{1/2} - \frac{2.3RT}{nF} \lg \frac{i}{i_d - i}.$$

The results of the graphical analysis of the waves of sexivalent uranium in the presence of quadrivalent vanadium, and in the absence of the latter, and also of the waves of trivalent vanadium, are given in Table 1; this table contains the mean values of the half-wave potentials $\varphi_{1/2}$ and the values of 2.3 RT/nF for the first wave of uranium at −0.2 volt and for the second, additional wave, at −0.5 volt.

TABLE 1

Combination of ions	First wave		Second wave	
	$\varphi_{1/2}$ b	2.3 RT/nF b	$\varphi_{1/2}$ b	2.3 RT/nF b
U^{VI}	−0,197±0,003	0,057±0,002	—	—
$U^{VI}+V^{IV}$	−0,194±0,005	0,056±0,002	−0,507±0,005	0,060±0,002
$U^{VI}+V^{IV}+V^{III}$	−0,199±0,003	0,056±0,001	−0,510±0,003	0,062±0,001
V^{III}	—	—	−0,504±0,004	0,062±0,002

It is evident from the table that the values of the half-wave potentials and the values of 2.3 RT/nF for the wave of uranyl in the presence of quadrivalent vanadium are the same as in the absence of the latter. This fact indicates that, in the presence of vanadium, the first wave corresponds – in agreement with published results [1-4] – to the reversible reduction of uranyl ions to quinquevalent uranium ions:

$$UO_2^{2+} + e \rightleftarrows UO_2^{+}.$$

The presence of trivalent vanadium in solution has no effect either on the half-wave potential or the height of this wave.

The second, additional, wave corresponds both with respect to position and in form to that of trivalent vanadium, i.e., in accordance with available published results [9, 10], it corresponds to the reversible reduction of trivalent vanadium to the divalent state:

$$V^{3+} + e \rightleftarrows V^{2+}.$$

Polarograms of solutions which contain trivalent vanadium in addition to uranium and quadrivalent vanadium, confirm this. At dropping electrode potentials approximating − 0.5 volt, only one clearly defined wave is observed.

On the basis of these results of graphical analysis, it can be concluded that since the uranium wave in the presence of quadrivalent vanadium corresponds to the reduction of sexivalent uranium to the quinquevalent state, the increase in its height is connected with the formation of additional amounts of UO_2^{2+} ions on the electrode surface; these UO_2^{2+} ions, together with trivalent vanadium ions, are formed in the neighborhood of the electrode as a result of chemical oxidation of quinquevalent uranium by quadrivalent vanadium, probably according to the reaction:

$$UO_2^{+} + VO^{+2} + 2H^{+} \rightleftarrows UO_2^{2+} + V^{3+} + H_2O.$$

The Oxidation-Reduction Reaction between Quinquevalent Uranium and Quadrivalent Vanadium. The possibility that such a reaction occurs is confirmed by results on oxidation-reduction potentials. The formal potential of the system U^{VI}/U^{V} in 0.1 N KCl and 0.1 N HCl is + 0.062 volt [11], while the value of the normal oxidation-reduction potential of the system V^{IV}/V^{III} is + 0.314 volt on the hydrogen scale [12].

In order to confirm the possiblity of an oxidation-reduction reaction between quinquevalent uranium and quadrivalent vanadium, quinquevalent uranium was titrated amperometrically with a solution of quadrivalent vanadium sulfate.

Quinquevalent uranium was prepared together with sexivalent uranium by reducing uranyl sulfate with hydrogen in the presence of smooth platinum; its concentration was determined from the height of the anodic part of the U^{VI}/U^{V} wave. Titration was carried out in 0.1 N KCl and 0.005 N HCl; at this concentration of hydrogen ions

in solution, quinquevalent uranium is most stable. As $VOSO_4$ solution was added, the height of the anodic part of the uranium wave decreased, while that of the cathodic part increased correspondingly: the total height of the anode-cathode wave remained constant throughout.

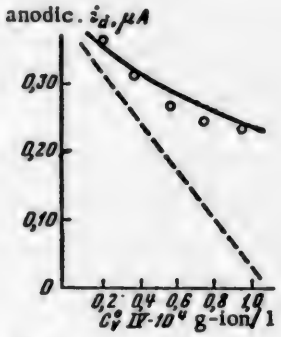

Fig. 1. Amperometric titration of quinquevalent uranium with $VOSO_4$.

In Fig. 1. is shown the results of such a titration carried out with a solution containing $1.07 \cdot 10^{-4}$ g-ion/ / liter of UO_2^+ and $0.91 \cdot 10^{-4}$ g-ion/ liter of UO_2^{2+}, and using a $0.5 \cdot 10^{-3}$ M solution of $VOSO_4$; the circles represent the values obtained experimentally for the anodic diffusion current, corrected for change in volume on addition of $VOSO_4$ solution. As Fig. 1 shows, these points lie on a curve, which, with increasing vanadium concentration, acquires a constantly decreasing slope. That the curve has this shape can be explained on the grounds that the reaction considered does not go to completion; the equilibrium state is already reached at considerable values of the concentration of UO_2^+ in solution. The dotted line is the theoretical curve for amperometric titration in the case where the reaction proceeds almost to the end, i.e., in the case where the diffusion current would be equal to zero, on addition of the equivalent amount of quadrivalent vanadium.

For the reaction

$$UO_2^+ + VO^{2+} + 2H^+ \rightleftarrows UO_2^{2+} + V^{3+} + H_2O$$

the numerical value of the equilibrium constant calculated from the values of the normal oxidation-reduction potentials (for $[H^+] = 5 \cdot 10^{-3}$), is equal to:

$$K = \frac{[UO_2^{2+}]\,[V^{3+}]}{[UO_2^+]\,[VO^{2+}]} = 1{,}6\,.$$

The expression for the equilibrium constant allows us to calculate the equilibrium concentration of UO_2^+ for any concentration of VO^{2+} added to the solution. When the initial concentrations of sexi- and quinquevalent uranium before starting a titration are C^0_UVI and C^0_UV, while the concentration of quadrivalent vanadium added is C^0_UIV. and X g-ion/ liter of V^{IV} reacts, then, in accordance with the equation for the reaction, the equilibrium concentrations will be expressed as follows:

$$C_U{}^{VI} = C^0_U{}^{VI} + X, \quad C_V{}^{III} = X,$$
$$C_U{}^{V} = C^0_U{}^{V} - X, \quad C_V{}^{IV} = C^0_V{}^{IV} - X.$$

Then, for the equilibrium constants, we can write:

$$K = \frac{(C^0_U{}^{VI} + X)\cdot X}{(C^0_U{}^{VI} - X)\,(C^0_V{}^{V} - X)} = 1{,}6.$$

Solving this quadratic equation with respect to X, we get the values of the equilibrium concentrations of quinquevalent uranium C_UV = C^0_UV − X and, consequently, the values of the anodic diffusion current for all values of C^0_VIV for the given original concentrations C^0_UVI and C^0_UV.

The continuous line in Fig. 1 represents the theoretical curve calculated in this way, for the amperometric titration of quinquevalent uranium with a solution of quadrivalent vanadium. As can be seen from Fig. 1, the experimental points lie quite satisfactorily on the theoretical amperometric titration curve, constructed by taking

into account the theoretically calculated equilibrium constants of the reaction; this seems to be confirmation of the possibility of the occurrence of an oxidation-reduction reaction between quinquevalent uranium and quadrivalent vanadium, as a result of which ions of sexivalent uranium and trivalent vanadium are formed.

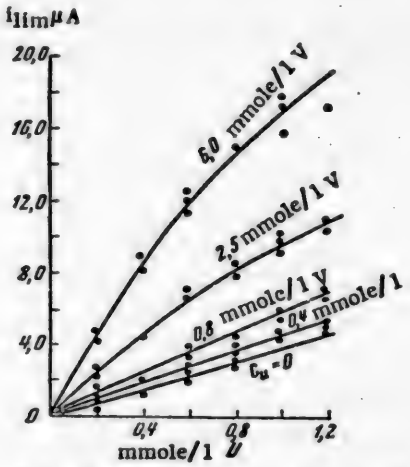

Fig. 2. Relation between the limiting current and uranium concentration.

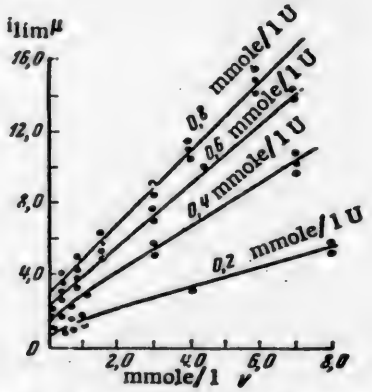

Fig. 3. Relation between the limiting current and vanadium concentration.

In the case of the reduction of sexivalent uranium in the presence of quadrivalent vanadium on a dropping electrode, all the sexivalent uranium formed as a result of chemical reaction on the electrode is reduced again on the electrode, thereby continuously supplying quinquevalent uranium ions for chemical reaction, and removing sexivalent uranium ions from the sphere of reaction; under such conditions, the rate of chemical reaction becomes high enough to effect an increase in the limiting current of uranium, which is several times greater than the diffusion current.

The phenomenon of an increase in the polarographic limiting current as the result of the occurence of a chemical reaction at the electrode surface is not a new one. Similar phenomena have been observed during the reduction on a dropping electrode, of trivalent iron ions in the presence of hydrogen peroxide [13], of sexivalent tungsten in the presence of perchloric acid [14], of quadrivalent titanium in the presence of hydroxylamine [15], and of the oxalate complex of titanium in the presence of ClO_4^- ions [16].

The Relation Between the Limiting Current and Uranium and Vanadium Concentrations. The relation between the limiting current and uranium concentration was studied over a concentration range up to 1.2 millimoles/liter for four values of the vanadium concentration in solution. The results are given in Fig. 2, where each curve corresponds to a definite constant concentration of vanadium.

The relation between the limiting current and vanadium concentration is shown in Fig. 1. Each curve represents the change in the limiting current as a function of vanadium concentration in the solution for a given uranium concentration. By studying the relation between the slope of the linear parts and the uranium concentration, an empirical equation was obtained which expresses the relation between the limiting current and the concentration of uranium and vanadium respectively:

$$i_{lim.current} = C_V (2.14 + \ln C_U) + K(C_U + 0.05),$$

where $i_{lim.current}$ is the limiting current, C_U is the uranium concentration, and C_V is the vanadium concentration; and K is the Ilkovich constant which is equal to $605\, n D_n^{1/2} \cdot m^{2/3} \cdot \tau^{1/6}$

The values of the limiting current calculated by means of this equation coincide satisfactorily with the values obtained experimentally over the uranium concentration range 0.2 to 1.2 millimoles/liter, and the vanadium concentration 1 to 8 millimoles/liter (at a temperature of 20° and a hydrochloric acid concentration of 0.05 N).

A study of the relation between the limiting current of the second, additional wave at −0.5 volt and the concentration of uranium and vanadium in solution, showed that the nature of this relation is identical to that

for differences between the limiting current of uranium in the presence of vanadium $i_{lim.current}$ and its diffusion current in the absence of the latter i_d. The difference $i_{lim.current} - i_d$ is a part of the total general current determined by the occurrence of a chemical reaction at the electrode surface. According to the equation given above for this reaction, sexivalent uranium and trivalent vanadium are formed in the layers near the electrode in equivalent amounts; therefore the difference $i_{lim.current} - i_d$ and the value of the limiting current of the second wave i', corresponding to the reduction of trivalent vanadium, can only differ from each other by a constant multiplier equal to the square root of the ratio of the diffusion coefficients of the UO_2^{2+} and V^{3+} ions. In Table 2 are given the values of the ratio $i'/i_{lim.current} - i_d$ for several different concentrations of uranium and vanadium in solution.

TABLE 2

c_U mmole/l	c_V mmole/l	$i_{lim} - i_d$ (μamp)	i'. μamp.	$i'/i_{lim} - i_d$
0,2	0,4	0,25	0,30	1,2
0,2	0,8	4,94	6,34	1,3
0,4	0,4	0,48	0,60	1,2
0,4	7,0	8,74	12,32	1,4
0,6	0,8	1,37	1,70	1,2
0,6	3,0	5,19	6,60	1,3
0,8	3,0	5,88	6,85	1,2

The values for $i'/i_{lim.current} - i_d$ can be regarded as constant (the mean value is equal to 1.2); the deviations observed are the result of errors in measuring the wave height.

Effect of the Acidity of the Solution on the Limiting Current. It is known from published results [17-19] that the disproportionation of quinquevalent uranium ions into hexa- and quadrivalent ions at the surface of the dropping electrode starts to affect the value of the limiting current appreciably at a hydrogen ion concentration in excess of 0.2 g-ion/liter. With increasing acidity of the solution, the disproportionation rate increases; a consequence of this is a continuous increase in the limiting current of uranium up to the point where the quinquevalent uranium formed on the electrode surface does not disproportionate completely, as a result of which the limiting current becomes a constant and is double the diffusion current of uranium in weakly acid solutions.

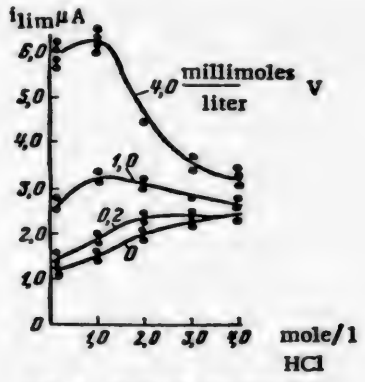

Fig. 4. Relation between limiting current and hydrochloric acid concentration.

When quadrivalent vanadium is present in a strongly acid solution, oxidation of quinquevalent uranium in the layers near the electrode by the ions of quadrivalent vanadium is superimposed on the disproportionation of quinquevalent uranium. In Fig. 4. is shown the relation obtained experimentally between the limiting current of uranium (0.4 millimoles/liter), both in the absence of vanadium, and in its presence (for three different vanadium concentrations), and the hydrochloric acid concentration of the solution. As this Fig. shows, the limiting current increases in all cases with increasing acid concentration up to an acid concentration of 1 N; the maximum value is reached at this point, thereafter there is a sharp drop with further increases in the acid concentration, and the value tends to the value for the limiting current in the absence of vanadium.

In all probability, with increasing acidity of the solution, the rate of oxidation of quinquevalent uranium increases; but, at acid concentrations in excess of 1 N, the rate of disproportionation of the quinquevalent uranium increases to a considerably greater extent, thanks to which there is also observed a drop in the value of the limiting current at high acid concentrations. This fact serves as indirect confirmation of the occurrence of a chemical

oxidation of quinquevalent uranium by quadrivalent vanadium in the layers near the electrode.

Effect of Temperature on the Limiting Current. The effect of temperature on the value of the limiting current for the reduction of uranium in the presence of vanadium, also indicates the occurrence of a chemical reaction on the electrode surface. At ordinary temperatures the rate of most chemical reactions increases by 2-3 times on increasing the temperature by 10°, while for diffusion processes the value of the temperature coefficient amounts to only 1.15-1.20. Thus measurements of the value of the temperature coefficient of the limiting current $i_{\text{lim.current } t+10} / i_{\text{lim.current } t}$ may indicate the occurrence of a chemical reaction in the layers near the electrode, the rate of which may partially or completely determine the value of the limiting polarographic current.

TABLE 3

C_V, μmoles/liter, t°	Temperature, in °C				
	0-10	10-20	20-30	30-40	40-50
0	1.18	1.15	1.13	1.12	1.10
0.2	1.33	1.25	1.20	1.17	1.14
1.0	1.58	1.36	1.27	1.22	1.18
6.0	2.06	1.53	1.35	1.26	1.20

A study of the relation between the limiting current and temperature was carried out in the temperature range 5-50°. The values of the temperature coefficients of the limiting current of uranium (0.4 millimole/liter) $i_{\text{lim.current } t+10} / i_{\text{lim.current } t}$ calculated from the experimental results, in relation to the temperature and vanadium concentration in solution, are given in Table 3.

The values for the temperature coefficients given in this Table indicate qualitatively that the limiting current for the reduction of uranium in the presence of vanadium, together with the diffusion process, is also determined by the rate of the chemical oxidation of quinquevalent uranium by quadrivalent vanadium which occurs on the surface of the droppping electrode.

We have learned that V. G. Sochevanov and N. V. Shmakov, as a result of work carried out by them in 1953, came to a similar conclusion regarding the mechanism of the effect of vanadium on the reduction of uranium on a dropping mercury electrode.

SUMMARY

1. A graphical analysis has been made of the polarographic wave obtained for sexivalent uranium in the presence of quadrivalent vanadium, as well as an analysis of a second, additional wave; as a result it has been found that the uranium wave corresponds to a reversible reduction of uranyl ions to quinquevalent uranium ions as in the case where no vanadium is present, while the additional wave corresponds to the reduction of trivalent vanadium to the divalent state.

2. On the basis of this graphical analysis of the polarographic waves of solutions containing uranium and quadrivalent vanadium, it has been shown that the reason for the increase in the uranium wave in the presence of vanadium is the occurrence on the dropping electrode surface of a chemical oxidation reaction of quinquevalent uranium by quadrivalent vanadium, the rate of this reaction, together with the diffusion process, are the determining factors for the value of the limiting current.

3. An amperometric titration of quinquevalent uranium with quadrivalent vanadium sulfate has demonstrated the possibility of such an oxidation-reduction reaction.

4. Results obtained during a study of the effect of the acidity and temperature of the solution on the limiting current confirm the occurrence of a chemical reaction in the layers near the electrode.

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AN ANALYTICAL STUDY OF THE PRECIPITATION OF QUADRIVALENT URANIUM BY SODIUM HEXAMETAPHOSPHATE

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Methods are known for the precipitation of uranium by means of the salts of ortho-, and pyrophosphoric acids and by hypophosphates [1-3]. An essential drawback of the gravimetric method based on precipitation of uranyl orthophosphate followed by calcination to the pyrophosphate, is the variable composition of the compounds formed. Precipitation with orthophosphate has only been used for separating uranium from certain elements, mainly from vanadium [4]. Uranium is quantitatively precipitated as its orthophosphate in weakly acid or weakly alkaline media. Consequently, the phosphate method can be used for separating uranium from a very limited number of elements. The specificity of the method can be increased in two ways: a) by establishing more specific conditions for the precipitation of sexivalent uranium, e.g., by addition of Complexon III [5]; b) by precipitating uranium in a mineral acid medium in a quadrivalent state. At present two variants of the method have been developed for ore analysis; they differ from each other in the method used for reducing U^{VI} to U^{IV} [6].

Collectors – thorium and zirconium phosphates – are used for isolating small amounts of uranium. It is possible that the sparingly soluble compound formed between hexametaphosphates and quadrivalent uranium may be of interest for separating small amounts of uranium.

Sodium hexametaphosphate has been used hitherto as a complexing agent [7-8].

Solutions of uranyl acetate were prepared for the work; they were standardized vanadometrically [9]. Uranium was reduced in a special semi-micro electrolytic cell using a current of 2 amps and 5 volts in the course of 30 minutes.

Sodium hexametaphosphate was obtained by heating sodium dihydrogen phosphate $NaH_2PO_4 \cdot 2H_2O$ in a platinum basin for 10-15 minutes at 620° and then rapidly cooling the melt formed. 2% aqueous solutions were prepared from the ground melt. Solutions of higher concentration could not be prepared in the cold.

The aqueous hexametaphosphate solutions show a neutral reaction and are fairly stable in the cold; nevertheless, on heating or on acidification, they hydrolyze [7, 10]. The sodium hexametaphosphate content of the solution which was shown to be 96.04% was established by titration with barium chloride [7]. Acidimetric titration and appropriate qualitative reactions showed that in a freshly prepared solution, pyro- and orthophosphates are almost absent; nevertheless they are gradually formed when the solution is allowed to stand.

Experiments showed that on addition of hexametaphosphate to an acid solution of quadrivalent uranium in the cold, no visible changes were evident. When, however, the solution was heated to 60-80°, a precipitate with a greenish color separated out. On increasing the temperature further, the volume of the precitate decreased appreciable, as was to be expected, while continued boiling led to the complete solution of the precipitate. It was also noticed that on addition of large amounts of sodium hexametaphosphate (e.g., 0.5 g) to 10-25 ml of solution containing 25 mg U, the latter was not precipitated either in the cold or on heating.

In order to establish the conditions necessary for the quantitative precipitation of uranium, a solution containing quadrivalent uranium, and sulfuric acid or perchloric acid, was heated on a water bath to a certain temperature, and a freshly prepared 2% solution of sodium hexametaphosphate added slowly, dropwise. The precipitate formed was kept on the water bath for a certain time, and then centrifuged; it was finally dissolved on heating in concentrated

sulfuric acid. The amount of uranium was determined vanadometrically.

A series of experiments showed that uranium is precipitated to the greatest extent by heating the solutions to 60-70° before precipitation (Table 1); after precipitation, it is necessary to heat the solution for 10-15 minutes on a water bath (Table 2).

TABLE 1

Effect of the Temperature of the Solution on the Precipitation of Uranium (24.04 mg of U taken)

Temperature, in °C	Volume of 0.02 N NH_4VO_3, in ml	U found	
		in mg	in %
18-20	–	Precipitate not formed	
60-70	9.35	22.25	92.76
100	8.10	19.28	80.20

TABLE 2

Effect of Duration for which Solution plus Precipitate are Heated on Completness of Precipitation of Uranium (24.04 mg U taken)

Time of heating, in minutes	Volume of 0.02 N NH_4VO_3, in ml	U found	
		in mg	in %
15	9.35	22.25	92.76
50	1.15	2.74	11.39
150	–	Precipitate dissolves completely	

In perchloric acid solutions, quadrivalent uranium is quantitatively precipitated over a narrow hydrogen ion concentration corresponding to 3 N (Fig. 1, Curve 2). The comparatively sharp decrease in the amount of uranium precipitated, with an increase or decrease in acidity on each side of this optimum acidity, is obviously connected, in the first instance, with the enhanced solubility of the compound formed as a result of the hydrolysis of the hexametaphosphate, and in the second case with the possibility of the formation of a complex compound of uranium.

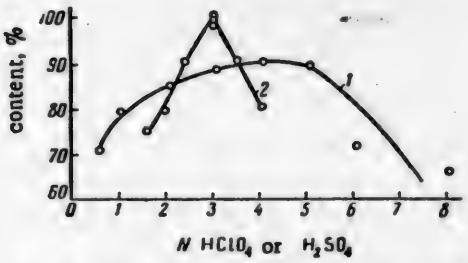

Fig. 1. Effect of acidity on precipitation of uranium with sodium hexametaphosphate. 1) Precipitation in H_2SO_4 media; 2) in $HClO_4$ media.

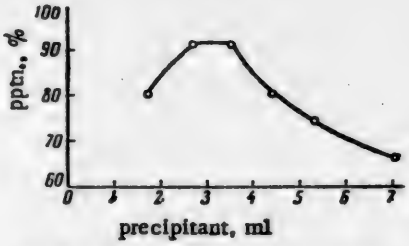

Fig. 2. Effect of the amount of hexametaphosphate on the precipitation of uranium in a medium of H_2SO_4.

Quadrivalent uranium is not completely precipitated in sulfuric acid solutions (Fig. 1, Curve 1); this fact has also been established by other research workers for the orthophosphate of quadrivalent uranium [6, 11], and is explained, presumably, by the formation of complex uranium compounds with the sulfate. Incomplete precipitation in sulfuric acid solutions was observed during a study of the effect of various amounts of sodium hexametaphosphate. It is clear from Fig. 2 that maximum precipitation of uranium occurs on adding 2.6-3.5 ml of a 2% solution of the precipitant when the total volume is 20 ml; this corresponds to a molar ratio of U : PO_3 = 1 : 6 - - 1 : 8.

In perchloric acid solutions, completeness of precipitation of uranium depends not so much on the molar ratio of uranium to hexametaphosphate as on the concentration of the latter in solution. Almost complete precipitation of more than 2 mg of uranium in 3 N perchloric acid is achieved at a final concentration of hexametaphosphate in solution of 0.30-0.35% (Table 3). Nevertheless, under the conditions indicated, a precipitate is not formed for uranium contents of about 0.2 mg in 20 ml of solution.

Thorium was used as a coprecipitant for isolating small amounts of uranium. It was established that addition

of 5 ml of 0.5% thorium chloride solution ensures complete precipitation of traces of uranium. Increasing the amount of coprecipitant does not lead to an increase in the amount of uranium precipitated, while at the same time it complicates further operations because of the large volume of precipitate. Uranium can be precipitated in the presence of thorium not only on heating, but also in the cold. For example, for contents of 2-3 mg uranium in solution, 99-100% of this element is precipitated, while for contents of 0.1-0.3 mg, the amount precipitated is about 70-80%. In the latter instance, in order to achieve complete precipitation, it is necessary to heat the solution to 60-70°. The possibility of precipitating small amounts of uranium together with thorium from a medium of 3 N $HClO_4$, has advantages over precipitation from 0.25-0.35 N HCl as the orthophosphate [6].

TABLE 3

Precipitation of Uranium by Hexametaphosphate in Perchloric Acid Solutions [$(NaPO_3)_6$ concentration 0.30-0.35%]

U taken, in mg	NH_4VO_3 used up, in ml	U found*	
		In mg	In %
24.04	10.05 (0.02 N)	23.01	99.46
2.53	10.68 (0.002 N)	2.54	100.40
2.53	10.60 (0.001 N)	2.52	99.60

* Mean of 3-4 determinations

The addition of hexametaphosphate in amounts greater than the molar ratio Th : PO_3^- = 1 : 5, leads to low results for uranium. Accordingly, the maximum amount of reagent corresponds to a 25% excess of it with respect to thorium, if it is assumed that $Th(PO_3)_4$ is formed.

TABLE 4

Behavior of the Precipitate Towards Various Wash Liquors

Wash liquor	Color observed	Mean value of D	U found, in g
Cold water	–	–	–
Hot water	+	0.027	0.0040
Water + C_2H_5OH in the proportion 1 : 1	–	–	–
Water + C_2H_5OH in the proportion 1 : 2	+	0.015	0.0021
Water + C_2H_5OH in the proportion 1 : 3	+	0.010	0.0015
$(NaPO_3)_6$ solution, 0.0025 g/ml	+	0.023	0.0020
$HClO_4$ solution (20 ml of acid in 1 liter of water)	–	–	–

* +) the solution is colored yellow
–) colorless solution.

In order to choose a suitable wash liquor, the precipitate of uranium obtained under the optimum precipitation conditions was shaken up with various wash liquors for 30 minutes at 20°. The precipitate was then centrifuged, and the uranium content of 5 ml of centrifugate determined photometrically by the peroxide method. Only the optical density of solutions which had a weak-yellow color was measured (Table 4).

When the precipitate was washed with cold water and with a mixture of water and alcohol, the precipitate was found to be peptized. When hot water or a dilute solution of sodium hexametaphosphate was used, appreciable amounts of the precipitate dissolved. The best wash liquor proved to be a dilute solution of perchloric acid (e.g., 0.01 N).

The method used for determining uranium may be stated concisely as follows:

20 ml of 3 N perchloric acid containing quadrivalent uranium* is heated to 60-70°. When not less than 2 mg of uranium is present, 3.5 ml of a freshly prepared 2% solution of sodium hexametaphosphate is added. In order to precipitate small amounts of uranium (tenths of a milligram), 5 ml of a 0.5% solution of thorium chloride solution is added, followed by precipitant solution in an amount which is 25% in excess with respect to the thorium. For improved coagulation of the precipitate, the solution is heated on a water bath for 10-15 minutes. The precipitate is centrifuged and then washed with 0.01 N perchloric acid; it is finally dissolved in 10-12 ml of concentrated sulfuric acid on heating. Uranium determination is finished vanadometrically.

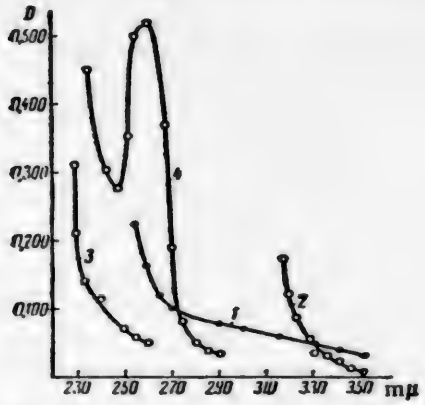

Fig. 3. Absorption curves for uranium solutions. 1) Perchloric acid solution of U^{VI}; 2) perchloric acid solution of U^{VI}; 3 and 4) perchloric acid solution of U^{IV}; in the presence of sodium hexametaphosphate.

TABLE 5

Precipitation of Uranium with Sodium Hexametaphosphate

U taken, in mg	U found, in mg	Error	
		in mg	in %
28,15	27,97	—0,18	—0,64
28,38	28,56	0,18	+0,63
28,38	28,44	+0,06	+0,21
28,38	28,08	—0,30	—1,06
2,02	2,02	0	0
2,02	1,98	—0,04	—1,98
2,02	2,05	+0,03	+1,49
0,250	0,249	—0,001	—0,40
0,250	0,252	+0,002	+0,80
0,190	0,190	0	0
0,190	0,191	0,001	+0,53
0,190	0,190	0	0

Under the conditions given above for the determination of uranium, tri- and quadrivalent vanadium (2-20 mg), iron, copper (up to 200 mg of each), and other di- and trivalent elements are not precipitated.

As noted above, under certain conditions, formation of complex compounds of uranium with hexametaphosphate is presumably possible. We have confirmed this possibility by carrying out a spectrophotometric study of the solutions. Using an SF-4 spectrophotometer, absorption curves were taken for quadri- and sexivalent uranium in the absence and in the presence of sodium hexametaphosphate, in amounts at which the uranium is not precipitated; namely, at ratios of $U : PO_3^- = 1 : 48$ for U^{IV} and $1 : 16$ for U^{VI}. The optical density of sodium hexametaphosphate solutions is zero in the region 225-290 mμ. The null solutions were 3 N perchloric acid solutions of sodium hexametaphosphate of the appropriate concentration.

On the basis of the results obtained, (Fig. 3), it can be concluded that U^{VI} and U^{IV} form complex compounds with hexametaphosphate. In the case of U^{VI}, on addition of hexametaphosphate, there is an increase in the optical density at the corresponding wave-lengths (Curves 1 and 2); while in the case of U^{IV} there is a change in the nature of the curve, with the appearance of a maximum on the absorption curve at 260 mμ (Curves 3 and 4).

SUMMARY

The possibility of precipitating quadrivalent uranium with sodium hexametaphosphate has been established. The effect of various factors on the completeness of precipitation of uranium has been studied. It has been found that complete precipitation can be effected from 3 N perchloric acid. Thorium has been used as a coprecipitant for the complete separation of small amounts of uranium.

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*Obtained by electrolysis on a mercury cathode.

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*Original Russian pagination. See C. B. Translation.

DETERMINATION OF TRACES OF COPPER IN AGRICULTURAL MATERIALS BY MEANS OF PAPER CHROMATOGRAPHY

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The chromatographic method has still not found sufficiently wide application in the analysis of agricultural chemicals. Several papers have been devoted to chromatographic studies of organic insecto-fungicides [1-6]. Due attention has not been given to the application of chromatography in the analysis of mineral preparations. At the same time, despite the large number of macro methods available [7], satisfactory methods have not yet been developed for determination of small amounts of "insecto-fungicide" ions (Cu^{2+}, Hg^{2+}, Ba^{2+}, Zn^{+2}, AsO_3^{3-}, AsO_4^{3-}, F^-, SiF_6^{2-}, CN^-) in agricultural materials (grain, fruit, leaves, etc.). Paperchromatography may be able to play an important part in solving this problem.

We have studied the possibility of using paper chromatography for the quantitative determination of traces of copper. We decided on using Cu^{2+} cations because copper-containing preparations (copper sulfate, preparation AB, Paris Green, copper oxychloride, Bordeaux Mixture, copper trichlorophenolate, copper naphthenate) are widely used in agriculture.

Of the methods published in the literature, for carrying out quantitative determination of materials located on paper [8, 9], of interest in the present endeavor were the following approximate, but simple and relatively rapid methods: a) direct comparison of the zones developed with chromatographic standards; b) methods based on the existence of a relation between the concentration of the test component and the area of its zone on the chromatogram:

$$S = a\text{Log}.c + b$$

where S is the area of the spot of the test component on the chromatogram; c is the concentration of the component in the original solution; a and b are empirical constants.

The latter method was suggested [10] for the quantitative study of amino acids. Its suitability for determining mineral ions by means of circular chromatograms has not been studied. Accordingly, it was necessary: 1) to examine the relation between the concentration of Cu^{2+} ions and the width of its localization zone on the developed circular chromatograms; to check on the reproducibility of the R_f values under the experimental conditions adopted. After this it should be possible to develop a technique for determining traces of copper in plant material.

Determination of R_f Values, and the Width of the Cu^{2+} Zones on Paper. Preliminary tests showed the correctness of Ivanova's conclusion that for the chromatographic separation of inorganic ions, the best filter paper is "blue band" paper. Accordingly, in the course of the work described here, circular ashless "blue band" filter papers TU MMP RSFSR No. 304-53 with a diameter of 12.5 cm were used exclusively. Solutions were prepared from chemically pure reagents and twice-distilled water.

In all cases, 0.05 ml of solutions containing various amounts of Cu^{2+} ions were placed on the center of the paper by means of a micropipet. The original spot thus formed was ringed with pencil, i.e., its position on the paper was fixed. After the paper had been dried, a "tongue" 40 mm long and 4 mm wide was cut in the paper.

The chromatographic cells used were desiccators in each of which was placed a crystallizing basin to serve as support for the filter paper. Tall crucibles containing the solvent were placed in the middle of the crystallizing basin.

The solvent used for developing the chromatograms was both simple and readily available: 90% by volume of 80% ethanol and 10% of 5 N hydrochloric acid. A chromatogram took 4 hours to run. The developer used for the Cu^{2+} ions was a 10% solution of $K_4[Fe(CN)_6]$.

For determining R(f) values, we took the boundary of the spot formed as the beginning of the path of the Cu^{2+} ions, while the outer boundary of the circular zone formed after development was taken as the end of the path. The path taken by the solvent front was taken from the center of the chromatogram, i.e., from the center of the filter. In this way about 200 chromatograms were taken; each value given below represents the mean of 3-4 determinations.

The technique adopted permitted the determination of 5 γ of Cu^{2+}, i.e., it possessed an accuracy sufficient for practical purposes.

Table 1 contains the R_f values, and the width of the circular zones of the Cu^{2+} ions for the concentration range 5-50 γ.

TABLE 1

Determination of R_f Values and the Width of the Cu^{2+} Zones

Amount of Cu^{2+} in γ placed on the filter	R_f value	Zone width, in mm
5	0.28	1.0
10	0.29	1.5
20	0.29	2.0
30	0.30	3.0
40	0.29	4.0
50	0.28	4.5

It is evident from Table 1 that under the experimental conditions used, the R_f value for Cu^{2+} ions is a constant. The deviations from the mean values given did not exceed ± 0.02-0.03.

For quantities of copper in the range 5-50 γ there was found to be linear relation between the concentration of the test ion and the width of its circular zone on the chromatogram. In each case it proved possible to construct a calibration curve for the approximate determination of Cu^{2+}. Thus, by working with circular chromatograms there is no need to calculate the area of the spot for the component located on paper. All the same, this quantitative method is only possible for relatively low concentrations of the test ion. We established that on placing appreciable (more than 100 γ) amount of Cu^{2+} ions on the paper, the relation is no longer linear. Thus, in the range 100 to 200 γ of Cu^{2+} ions, the zone width only increases from 5 to 7 mm, i.e., by only 2 mm. Consequently, for quantities of the order to 100 γ and more of copper, determination of the latter on the basis of the zone widths of circular chromatograms is difficult.

TABLE 2

Chromatographic Determination in Agricultural Materials

Cu^{2+} taken, in γ	Cu^{2+} found, in γ
5	5
9	10
12	15
15	15
23	25

TABLE 3

Concentration of Solutions for Preparation of Chromatograms

No.	$CuSO_4 \cdot 5H_2O$ concentration, in g/liter	Amount of Cu^{2+} ions in 0.05 ml of the solution prepared, in γ
1	0.393	5
2	0.786	10
3	1.572	20
4	2.358	30
5	3.144	40
6	3.930	50

Description of the Method. The relationship found was used for the quantitative determination of traces of copper in agricultural materials (grain, fruit, leaves). First, known amounts of some copper-containing preparation (AB, cupric sulfate, Paris Green, etc.) were placed on some plant material. When this was done the copper dosage used was known to be less than that adopted in actual practice. For example, the amount of preparation AB actually placed on the plant material was equivalent to 1 kilogram per ton of wheat grain, although in agricultural practice larger amounts are used – up to 2.5 kilogram per ton. In this way we took into account natural losses of copper.

The amount of Cu^{2+} ions was then determined on the various plant materials by the chromatographic method described. The results obtained (Table 2) show that this approximate method is applicable for practical purposes.

Analytical Procedure. Before carrying out an analysis, it is essential to prepare chromatographic standards and construct a calibration curve on their basis. For this purpose, a series of chromatograms with successively increasing amounts of copper ions 10, 20, 30, 40, and 50 γ are taken. The concentrations of the copper solutions are shown in Table 3.

Six "blue band" filter papers 12.5 cm in diameter are taken and 0.05 ml of one of the copper solutions indicated above placed on the center of the paper. The solution is not poured onto the paper, but allowed to leak out by capillary action.

The filters are dried and the "tongues" cut out of them, 4 mm wide and 40 mm long. The "tongue" should be marked out on the filter paper with a pencil before placing the solution of copper ions on it. The desiccators used as chromatographic tanks are opened, and the "tongues" of the filter papers placed in crucibles containing solvent (10 ml), the crucibles being placed in the middle of crystallizing basins contained in the desiccators. The lids of the desiccators are replaced and the chromatograms allowed to run.

The developer used is a mixture containing 90% by volume of ethanol and 10% 5 N hydrochloric acid. Developing of the primary chromatogram with this solvent takes 4 hours. The filter papers are then removed from the desiccators, the solvent allowed to evaporate, and the papers developed by spraying them with 10% $K_4[Fe(CN)_6]$ solution from a glass sprayer (metallic ones are not suitable).

When the filter papers have been dried, the widths of the brown-red rings of Cu^{2+} are measured on each paper, and a calibration curve constructed on the basis of the results obtained. It is useful to keep the standard chromatograms, since during determination of very small amounts of copper (5-10 γ) the intensity of the color of the circular zones is of some significance.

When preparing the calibration curve, and also in carrying out an actual analysis, it is essential to observe strictly the conditions used for preparing the chromotograms. All operations should be carried out in exactly the same way. Desiccators, crystallizing basins, beakers, and filters should all be of the same size. The same micropipet should be used in all cases.

In order to get comparable results, strict observance of the dimensions of the "tongues" is of essential importance; the distance between the surface of the filter paper and the level of the solvent in the crucible is of equal importance. When the standard chromatograms have been obtained and a calibration curve constructed, analysis of the test samples is carried out.

All copper-containing agricultural materials (cupric sulfate, preparation AB, Paris Green, Bordeaux Mixture, copper oxychloride) readily dissolve in hydrochloric acid. Accordingly, 1-5 g of test material, treated beforehand with a copper-containing material — e.g. grain dusted with preparation AB — is washed with 2 N HCl, taking as a basis 1 ml of acid per gram of test material. The solution obtained is filtered through ashless "blue band" paper free from copper. 0.05 ml of this solution is then placed on the center of a filter. The chromatogram is allowed to run, and developed, etc., exactly as in the case of preparation of standards. The width of the zone is then measured, and, using the calibration curve, the approximate copper content determined.

The method described is only suitable for determining copper on the surface of plant material.

It is very useful to be able to identify the copper-containing preparations on the basis of chromatographic standards prepared once and for all and stored in the laboratory. For this purpose 100 mg aliquots of test material (AB, Paris Green, etc.) are dissolved in 5 ml of 2 N HCl, the solutions filtered and chromatographic standards obtained for each preparation as described above.

By choosing the appropriate solvent and developer, it should be possible to use paper chromatography for the determination of residual amounts of other ions (Hg^{2+}, Ba^{2+}, Zn^{2+}, AsO_3^{3-}, AsO_4^{3-}, F^-, SiF_3^{2-}, CN^-) on agricultural materials.

SUMMARY

1. R_f values have been determined for Cu^{2+} ions during chromatographic separation on "blue band" paper, using the following solvent: 90% (by volume) of 80% ethanol and 10% of 5 N hydrochloric acid (by volume).

2. It has been shown that within the limits of 5 to 50 γ of Cu^{2+}, there is a reasonably linear relation between concentration of copper ions and the width of the circular zones obtained on the chromatograms.

3. A new method has been developed for the determination of small amounts of copper in agricultural materials by means of paper chromatography.

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FORMATION OF SULFONIUM SALTS AS A METHOD FOR THE DETERMINATION OF ORGANIC SULFIDES

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For the quantitative determination of organic sulfides a number of authors [1-3] have used the capacity of the sulfides to react with bromine or iodine. In other methods [4-6] solutions of potassium iodate or of potassium bromide-bromate have been used for titrating the sulfides. The reaction of sulfides with heavy metal salts has also been employed by many authors [7-10]. The most suitable reagent for the quantitative extraction of sulfides is mercurous nitrate. The presence of unsaturated or aromatic compounds makes quantitative determination of sulfides impossible. At the same time, the determination of sulfides in petroleum products and in other complex mixtures is of considerable interest from the point of view of controlling technological processes and for developing methods of desulfurizing oils and motor fuels.

Organic sulfides are capable of forming sulfonium compounds according to the following scheme:

$$R_1 - S - R_2 + R_3 - Hal \rightarrow [R_1 R_2 R_3 S]^+ Hal^-$$

The compounds obtained are readily soluble in water, and, in aqueous solutions, prove to be typical electrolytes.

After sulfonium compounds had been discovered [11] numerous representatives of this class of compounds were prepared; nevertheless, the conditions under which they are formed have not been studied enough.

Carrara [12] while studying the rate of formation of triethylsulfonium iodide, found that the reaction was not quantitative under the experimental conditions he used. Ray and Levine [13], showed that for stoichiometric proportions of sulfide and the alkyl iodide, the reaction only went 50% of the way; at the same time complicated side-reactions leading to the formation of hydrocarbons and free iodine were found to occur. Bost and Everett [14] established that formation of sulfonium salts proceeds readily in a methanol medium. Hellstrom [15] showed that the reaction slows down in acid media. It follows from the papers quoted that formation of sulfonium salts proceeds best with methyl iodide in a methanol medium.

The aim of the work described here was to develop a method for the quantitative determination of organic sulfides on the basis of the formation of sulfonium compounds.

On heating a mixture of organic sulfide and methyl iodide in methanol at 100°, in a sealed ampoule, formation of the sulfonium compound proceeds quantitatively. Organic sulfides can be determined by heating a mixture of test samples, containing up to 0.5 millimole of sulfides, with 3-5 ml of methanol and about 5 millimoles of methyl iodide (ten times the expected amount of sulfides) in a thick-walled ampoule at 100° for 2-3 hours. The reaction mixture is then transferred from the ampoule to a separating funnel, and the ampoule rinsed out with water; the washings are added to the reaction mixture in the separating funnel. The unreacted methyl iodide is removed from the aqueous layers, and the aqueous solution extracted first with chloroform and then with ether for extraction of free iodine and methyl iodide residues. The aqueous solution is then transferred to a 250 ml standard flask. 50 ml of this solution is taken for titration and 10 ml of 0.05 N silver nitrate added; the mixture is then heated to the boil. The solution is diluted with water to about 100 ml, when a few mls of concentrated nitric acid is added and the whole boiled again to coagulate the silver iodide.

Excess silver nitrate is finally titrated with 0.05 N ammonium thiocyanate using ferric alum as indicator. In another aliquot of the same solution (50 ml), the hydrogen iodide formed is determined by titration with 0.05 N sodium hydroxide, using methyl red as the indicator. The organic sulfide sulfur content is calculated by means of the formula:

$$\%\, S_{sulfide} = \frac{0.05(a-b)\cdot 32.07\cdot 5\cdot 100}{100\cdot K},$$

where a is the amount of 0.05 N silver nitrate used up, in mls; b is the amount of sodium hydroxide used up, in mls; and K is the weight of the sample taken, in g.

Results for the determination of various individual organic sulfides are given in Table 1.

TABLE 1

Determination of Individual Sulfides

Sulfides	Amount taken, in moles · 10^{-3}	Found		Deviation, in %
		moles · 10^{-3}	in %	
Diallylsulfide	0.756	0.747	98.7	−1.3
		0.749	98.9	−1.1
Diisobutylsulfide	0.420	0.419	99.7	−0.3
		0.421	100.3	+0.3
Dipropylsulfide	1.171	1.175	100.2	+0.2
		1.176	100.3	+0.3
Dibenzylsulfide	0.416	0.417	100.1	+0.1
		0.420	100.0	+1.0

Thiophene, thianthrene, and diphenylsulfide do not give sulfonium salts.

Results for the determination of organic sulfides in gasolines are given in Table 2.

TABLE 2

Determination of Organic Sulfides Added to Gasolines

Composition of the mixture	Amount taken, in moles · 10^{-3}	Found		Deviation, in %
		moles · 10^{-3}	in %	
Petroleum-cracking gasoline and dipropylsulfide	0.1888			
Diallylsulfide	0.0494			
Diisobutylsulfide	0.0596			
Total:	0.2978	0.2971	99.8	−0.2
Fraction of shale gasoline 145-160°, and dipropyl-sulfide	0.1461			
Diallylsulfide	0.0781			
Diisobutylsulfide	0.0491			
Total:	0.2733	0.2682	98.4	−1.6

Anosile, guaiacol, and tricresol do not affect determination of organic sulfides. The method does not give correct results in the presence of mercaptans. In this case, more complicated reactions occur, e.g.:

$$R - SH + CH_3I \rightarrow R - S - CH_3 + HI \quad R - S - CH_3 + CH_3I \rightarrow \left[\begin{matrix} R - S - CH_3 \\ CH_3 \end{matrix}\right] + I -$$

Accordingly, for determination of organic sulfides by the method described it is necessary to remove mercaptans beforehand.

SUMMARY

A method has been developed for the determination of organic sulfides, which is based on the formation of sulfonium salts with an alkyl iodide.

It has been shown that this method can be used for the determination of individual organic sulfides in the presence of unsaturated and oxygen-containing compounds.

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DETERMINATION OF KETONES, ESTERS, AND ACIDS IN THE PRODUCTS OBTAINED BY LIQUID-PHASE OXIDATION OF PARAFFIN HYDROCARBONS, ON THE BASIS OF THEIR ABSORPTION SPECTRA IN THE INFRARED

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Chemical methods of analyzing the products from the liquid-phase oxidation of paraffin hydrocarbons are fairly complicated, and, in individual cases, particularly for the oxidation products of high-molecular hydrocarbons, analysis for ketones and esters does not always give correct results. Accordingly, we have studied the possibility of using infrared spectroscopy for the quantitative analysis of such mixtures. The published methods [1-2] of functional analysis of mixtures of oxygen-containing derivatives on the basis of their absorption spectra in the infrared have a number of drawbacks; they are either not accurate enough or are only applicable in the absence of carboxylic acids. The latter circumstance does not permit the use of these methods for the analysis of the oxidation products of unsaturated hydrocarbons, the acid content of these oxidation products, as a rule, being high.

In the work described here we have tried to develop a method for the quantitative determination of ketones, esters, and acids which would be reasonably accurate, and rapid to carry out, such as that required for kinetic studies, and also for the practice of oxidation of high molecular weight hydrocarbons of the paraffin series.

The spectra were registered on an IKS-11 apparatus with a sodium chloride prism. The apparatus was provided with a setup for automatically operating the slit, and also included an amplifier for registering the spectra by means of the EPP-09 recorder [3]. The cuvettes were of a type that prevented evaporation of the solvent during registration of the spectra [4]. The accuracy of determination of the position of bands in the 1700 cm^{-1} region was ± 3 cm^{-1}.

Calculation of the concentration C was carried out on the basis of the Lambert-Beer equation, the applicability of which was checked for all derivatives; $C = D/Kl$, where D is the optical density (D = logarithm (I_0/I)).

Here the intensity I_0 of the ray passing through the solvent is found by a method described earlier [4]; I is the intensity of the ray passing through the test solution; l is the thickness of the cuvette. The value of K was determined without taking into account apparatus corrections, so that it is necessary when working with other apparatus to carry out preliminary calibration with the test materials used. The materials whose spectra were taken were of varying origins:

a) Acetone, methyl ethyl ketone, dibutyl ketone, ethyl acetate, amyl acetate, and butyric and stearic acids were the commercial products purified by distillation or recrystallization.

b) Stearone was synthesized [5] from stearic acid, and was purified by a threefold crystallization from alcohol; m.p. 86.4° (published value 88.4°).

c) Methyl stearate was synthesized [5] from commercial stearic acid, and was purified by distillation under vacuum.

d) The synthetic fatty acids of varying composition were mixtures mainly of normal carboxylic acids containing small amounts of isocarboxylic acids; they were obtained by oxidation of mixtures of high-molecular weight paraffins at the SZhK combine in Shebenko. Various fractions of these acids were used; these fractions were obtained both by fractional distillation and by precipitation as their urea complexes. The composition of the fraction

is approximately determined by the distillation range.

e) The methyl esters of the synthetic acids were prepared by using the cation exchange resin PFSK [6], and were purified by fractional distillation.

TABLE 1

Class of material	Name	Molecular weight	Absorption coefficient, k, $m^{-1}cm^{-1}$	Band width, in cm^{-1}	Frequency $cm^{-1}\nu$	Solvent
Ketones	Acetone	58	310	15	1719	CCl_4
	Dibutylketone	142	310	17	1716	Heptane
	Methyl ethyl ketone	72	290	18	1722	CCl_4
	Heptanone-2	114	290	16	1719	CCl_4
	Stearone	508	320	14	1715	$CHCl_3$
	Mixture of ketones in oxidized paraffin (saponified)	–	–	18	1719	CCl_4
	Ketones (mixture)	249	280	17	1718	CCl_4
Esters	Ethyl acetate	88	520	–	1740	CCl_4
	Amyl acetate	130	486	14	1740	CCl_4
	Ethyl capronate	144	500	–	1744	Cyclohexane
	Ethyl stearate	298	500	14	1742	"
	Methyl esters of mixed acids $C_{14}-C_{18}$	338	511	20	1740	"
	Esters of C_{13} alcohol and $C_{14}-C_{16}$ acids	432	488	18	1736	"
Acids	Butyric acid	88	820	14	1712	Heptane
	n-Valeric acid	102	790	15	1712	CCl_4
	Stearic acid	284	780	14	1712	CCl_4
	Normal acid $C_{10}-C_{18}$	243	820	14	1709	CCl_4
	Normal acid C > 21	330	820	–	1709	CCl_4
	Mixture of acids $C_{10}-C_{18}$	247	670	18	1713	CCl_4
	Mixture of acids $C_{14}-C_{18}$	228	677	–	1713	CCl_4
	Mixture of acids C_7-C_9	156	700	16	1711	CCl_4
	Mixture of acids C_5-C_9	133	729	16	1714	CCl_4
	Mixture of "iso" acids $C_{10}-C_{18}$	206	583	21	1714	CCl_4
	Mixture of "iso" acids C > 21	266	640	21	1713	CCl_4

f) Esters of the synthetic fatty acids and C-13 alcohol: C-13 alcohol is the designation for a mixture of primary alcohols obtained by hydrogenation, by means of Adkins' [7] catalyst, of a narrow fraction of the methyl esters of the synthetic acids. The mean equivalent weight of these alcohols is 198; this corresponds to an alcohol with 12.9 atoms of carbon. The esters of this alcohol and the fatty acids from the C-14 and C-16 fractions were prepared by esterification in the presence of the cation exchange resin PFSK, and were purified by distillation under high vacuum.

g) Ketones (mixtures) with a mean molecular weight of 249 were obtained by oxidation of VZHS secondary alcohols with chromic anhydride, with subsequent purification and distillation under high vacuum.

The characteristics of the test materials used are given in Table 1.

Let us consider analysis in the presence of materials containing one > C = O group in the mixture.

For the purposes of quantitative functional analysis it is possible to use those absorption bands which preserve their characteristic frequency in a homologous series, and also exhibit constant absorption coefficients. Published results [8-9] as well as our own, permit one to conclude that the absorption bands of the carbonyl groups of ketones, esters, and acids, satisfy these requirements to a considerable extent. The absorption band for the C=O group in aliphatic ketones has a frequency of 1718 ± 3 cm^{-1}, while for the esters and acids the frequencies are respectively 1738 ± 3 cm^{-1} and 1713 ± 2 cm^{-1}.

The absorption coefficients which we established (Table 1) indicate that they are constant within the group of acids, esters, and ketones, since changes in their value do not exceed ± 2.5-3% of the mean value. When one bears in mind that, during the analysis of mixtures the experimental errors for all the components will be meaned it can be considered that variations in the absorption coefficients will give an error less than this.

In the case of one of the simplest cases of functional analysis of mixtures consisting only of esters, acids, or ketones, the molar extinction of such a mixture will be somewhat different from that of an individual compound. We shall find the value of this difference which is introduced because of incomplete agreement with respect to the frequencies of the carbonyl bands of the components of one homologous series.

The absorption coefficient of the carbonyl band for a mixture of materials can be calculated if the contours of the bands of the individual materials are known.

It has been shown that for many compounds, the contour of the carbonyl band is described quite well by the Lorenz equation [10]

$$D = \frac{a}{(\nu - \nu_0)^2 + b^2}. \qquad (1)$$

where ν_0 is the band frequency at the maximum; ν is the frequency of contour point; a and b are constants; and D is the optical density.

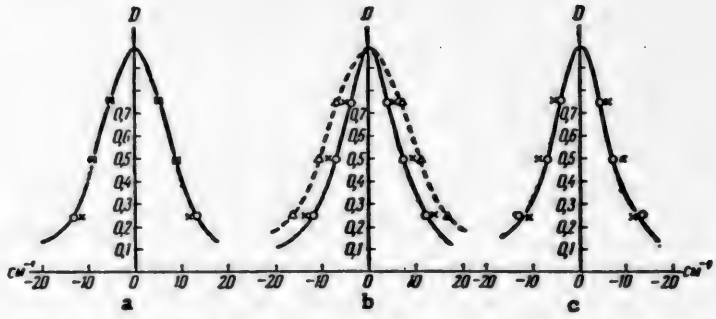

Fig. 1. Contours of the absorption band of the > C= O bond (values determined from the spectrograms):
a) Methyl ethyl ketone; o) individual methyl ethyl ketone;
x) ketones in oxidized paraffin (values found from the spectrograms);
b) stearic acid; o) individual stearic acid; x) $C_{10}-C_{16}$ acids;
Δ) contour of $C_{10}-C_{16}$ "iso" acids; c) methyl stearate; Δ) individual methyl stearate; x) esters of C_{13} alcohol and $C_{14}-C_{16}$ acids.

The contours which we obtained by means of the IKS-11 apparatus for the carbonyl bands of ketones, esters, and acids, are also satisfactorily described by this equation with constants which are constant within each group of materials. In Fig. 1 are shown the contours of carbonyl groups calculated by means of equation (1) and calculated from the spectrograms. Optical density is plotted along the ordinate – the optical density at the maximum being taken as unity – while the width of the contour, in reciprocal centimeters, is plotted along the abscissa.

From equation (1), and using the Lambert-Beer law, we get:

$$K = \frac{a}{(\nu - \nu_0)^2 + b^2} \qquad (2) \qquad \text{where} \qquad \alpha = \frac{a}{Cl}$$

Let us assume further that we have n + 1 materials with equal absorption coefficients, for which the position of the carbonyl bands is displaced relative to one another by the same amount equal to $\frac{\Delta\nu}{n}$, and that all the bands are located in the frequency range $\nu_0 - \frac{\Delta\nu}{2}$, $\nu_0 + \frac{\Delta\nu}{2}$. At the point ν_0 the optical density of the total absorption band will be given by:

$$D = \sum_i D_i = l \sum K_i C_i,$$

where K_i is the absorption coefficient of the i'th band at a frequency of ν_0; C is the concentration of each component.

The total absorption coefficient K is determined from the equation:

$$l \Sigma K_i C_i = K_0 l \Sigma C_i,$$

from which the absorption coefficient of the mixture is given by $K_0 = \Sigma K_i C_i = \frac{1}{C_0} \Sigma K_i C_i$.

Since, during liquid-phase oxidation of high-molecular weight hydrocarbons, a wide selection of compounds with various functional characteristics is obtained, in order to obtain K_0 in an integral form, we shall consider the case where $n \to \infty$. For this purpose, we shall determine the distribution function of the concentration of the materials according to the frequencies of the carbonyl band:

$$C_\nu = \varphi(\nu) d\nu.$$

Here, $\varphi(\nu)$ is the distribution function, and C_ν is the molar concentration of the components of the mixture in which the frequencies of the carbonyl bands lie within the limits ν, $\nu + d\nu$, then

$$K_0 = \frac{1}{C_0} \sum K_\nu \varphi(\nu)\, d\nu = \frac{1}{C_0} \int_{\nu_0 - \frac{\Delta\nu}{2}}^{\nu_0 + \frac{\Delta\nu}{2}} \frac{a\varphi(\nu)\, d\nu}{(\nu - \nu_0)^2 + b^2}.$$

Thus, determination of the mean value of the absorption coefficient reduces to establishing the distribution function $\varphi(\nu)$.

As tests have shown, during analysis of the products of liquid-phase oxidation of high-molecular weight paraffins with a reasonable degree of accuracy, it can be assumed that the distribution of components according to the frequencies of the carbonyl band is of equal probability, i.e.

$$\varphi(\nu) = \frac{C_0}{\Delta\nu} = \text{const},$$

then

$$K_0 = \frac{1}{\Delta\nu} \int_{\nu_0 - \frac{\Delta\nu}{2}}^{\nu_0 + \frac{\Delta\nu}{2}} \frac{a\, d\nu}{(\nu - \nu_0)^2 + b^2}.$$

By integrating, and resolving into series, we get:

$$K_0 = \frac{2a}{b\Delta\nu} \operatorname{arctg} \frac{\Delta\nu}{2b} = \frac{2a}{b\Delta\nu} \left[\frac{\Delta\nu}{2b} - \frac{\Delta\nu^3}{24b^3} + \cdots \right] =$$

$$= \frac{a}{b^2} \left[1 - \frac{\Delta\nu^2}{12b^2} + \cdots \right] = K \left[1 - \frac{\Delta\nu^2}{12b^2} - \cdots \right], \qquad (3)$$

where K is the absorption coefficient of an individual material. For $\Delta\nu = 5\ cm^{-1}$ and $\underline{b} = 8\ cm^{-1}$, we get

$$K^0 = K\left(1 - \frac{2.5}{64} - \frac{1}{512} \ldots\right) = 0{,}962\,K.$$

Thus, for the values of K we are considering: they can be expressed with a reasonable degree of accuracy by just the first two members of the resolution, and even in this case, the total absorption coefficient of the mixture will only differ by 4% from the absorption coefficient of an individual material. It is obvious that for any other form of the distribution function of the concentrations of the components, as long as it is symmetrical with respect to point ν_0, and does not have a minimum (this is usually fulfilled), the difference between K_0 and K will be even smaller.

TABLE 2

Test material	K-absorption coefficient, in $M^{-1}L\ cm^{-1}$	$K_{calc.}$ $M^{-1}L\ cm^{-1}$	b, in cm^{-1}	$\Delta\nu$, cm^{-1}
Ketones	300	288	9	6
Esters	500	470	7	6
Acids	780	755	7	4

Table 2 contains the values for the absorption coefficients of ketones, esters, and acids, meaned for several individual compounds calculated according to formula (3), and also the values of $\Delta\nu$ and $\underline{b}$; the latter remain constant in each series of functional derivatives.

During the oxidation of certain types of natural paraffin, in addition to acids with a normal structure, up to 30% of "iso" acids [11, 12] are formed, the carbonyl group of which has a lowered value for the absorption coefficient (Table 1) and a widened band contour (Fig. 1). At the same time the absorption coefficients of acids with "normal structure", isolated from the mixture of oxidation products, have values similar to those of the absorption coefficients of individual acids, and their contour coincides with the contour of stearic acid. As a consequence of the presence of "iso" acids, all the mixture of acids formed during oxidation has an absorption coefficient which is lower than the value determined by means of formula (3). This fact must be borne in mind when analyzing mixtures with appreciable amounts of "iso" acids.

In order to carry out an analysis, a sample of material $\underline{m}$ is dissolved in a known volume of CCl_4 or cyclohexane. The volume of solvent is chosen so that the optical density of the carbonyl band lies within the limits 0.3-0.6, in order to ensure the minimum experimental error. The optical density in the maximum of the band is found from the spectrograms taken in the 1700-1750 cm^{-1} region, while the molar concentration of material in the solvent (C) is calculated by means of the Lambert-Beer equation. The concentration C of the carbonyl-containing material in the original mixture is calculated by means of the equation:

$$C_n = \frac{C\nu}{m}\ \text{millimoles/g.} \qquad (4)$$

where C is the concentration in the solvent, and ν is the volume of solvent.

Determination of the concentration of ketones in the oxidation products of hydrocarbons is usually complicated when acids are present, since the absorption band of the carbonyl group of the acids is superimposed on the absorption band of the ketones. Analysis, is, however, possible, if, after determination of the optical density of the carbonyl band at the frequency of the ketone carbonyl group, a correction is made for absorption arising out of the presence of the carbonyl group of the acids.

Actually, for two superimposed absorption bands, we have:

$$D_{total} = D_{K-T} + D_K\,.$$

from which

$$C_K = \frac{D_{total}}{K_K l} - \frac{K_{K-T}}{K_K}\,C_{K-T}\,. \qquad (5)$$

Here K_K is the absorption coefficient of the ketone carbonyl band at the maximum point of this band, while K_{K-T} is the absorption coefficient of the carbonyl group of the acids at the same frequency; C_K and C_{K-T} are molar concentrations. Analysis of materials in cases where there occurs superposition of bands is fairly common in spectroscopic practice. This problem is most easily solved when the contours of the superimposed bands are known. In our case the band contours are described quite well by the Lorenz equation, right up to distances from 15-20 cm^{-1} from the center of the band. Since the distance between the centers of the carbonyl bands of ketones and acids is, on an average, equal to 5 cm^{-1}, the equation is used in order to determine the correction factor. At the band center, when $\nu = \nu_0$, we have

$$K_{max} = \frac{a}{b^2}.$$

Dividing equation (2) by this expression, we get:

$$K/K_{max} = \frac{1}{1+\left(\frac{\nu-\nu_0}{b}\right)^2}. \qquad (5a)$$

We then place

$$K/K_{max} = \eta; \qquad \frac{\nu-\nu_0}{b} = \zeta,$$

whence

$$\eta = \frac{1}{1+\zeta^2}. \qquad (6)$$

Formula (6) is the equation for the contour in dimensionless coordinates, the origin of which is related to the center of the band. The frequency shift from the center of the band, expressed in b units, is an independent variable, and is nothing else but the half-width of the contour at the point $D = D_{max}/2$. For mixtures of acids, $b = 9$ cm^{-1}, while the distance from the center of the band to the maximum point of the ketone band is equal to 5 cm^{-1}. Consequently, $\eta = 0.75$. $K = 585$ $m^{-1}L$ cm^{-1} at the maximum of the ketone band.

Having registered the spectra of the mixture of ketones and acids in CCl_4 solution (or other suitable solvent), and having found D_{total} from equation (5), the concentration is calculated; the acid content is determined beforehand by titration of the mixture, while acid content in the carbon tetrachloride is determined by calculation. The content of ketones in the original mixture is finally calculated by means of equation (4).

The absorption coefficient of the acids is considerably smaller than that of the ketones; this lowers the accuracy of the analysis when large concentrations of acids are present. Accordingly, it is interesting to know the ratio of the concentation of acid to ketones, for which it is expedient to carry out an analysis.

From equation (5), we have:

$$\Delta C_K = \frac{\Delta D_{total}}{K_K l} + \frac{K_{K-T}}{K_K}\Delta C_{K-T}. \qquad (7)$$

Assuming that the error in determining C_{K-T} by titration is 3%, while the error in determining the optical density ΔD is equal to 0.005, we can find what should be the ratio C_{K-T}/C_K so that the ketone can be determined with an accuracy of up to 10%. For a value of $D = 0.5$ for the optical density of the ketone band, the first member in expression (7) does not exceed 1%, when the total error is of one order higher. Disregarding this, therefore, we get:

$$0.1C_K = \frac{K_{K-T}}{K_K} \cdot 0{,}03\ C_{K-T}$$

or

$$C_{к.т} = 1.70\,C_к,$$

i.e., in order to determine ketone concentration with an accuracy of up to 10%, the concentration of acid in the mixture should not exceed that of the acetone by more than one and a half times.

For the determination of the concentration of ketones and esters when present together, analysis reduces to a calculation of the mutual correction for the superposition of the bands of the compounds. The carbonyl bands of esters have a frequency of 1738 ±3 cm^{-1}, while those of the ketones have a frequency of 1718 ± 3 cm^{-1}; the distance between these bands is equal to 20 cm^{-1} on the average. The absorption coefficients of ester carbonyl in the ketone region, and on the other hand of ketone carbonyl in the ester region, can be found by means of equations (5a) and (6). Using equation (5) which is applicable in the given instance, we have:

$$C_к = \frac{D_к - \eta_E K_E C_E l}{K_к l} \qquad C_к = \frac{D_к - \eta_E D_E}{K_к l}$$

$$C_E = \frac{D_E - \eta_к K_к C_к l}{K_E l} \qquad C_E = \frac{D_E - \eta_к D_к}{K_E l}.$$

Here C_K, C_E, K_K, and K_E are the concentrations and absorption coefficients of ketone and ester respectively; l is the cell thickness; D_K and D_E are the optical densities of the carbonyl bands in the ketone and ester regions respectively. Solving these equations, we get:

$$C_к = \frac{D_к - \eta_E D_E}{K_к l(1 - \eta_E \eta_к)}; \qquad C_E = \frac{D_E - \eta_E D_к}{K_E l(1 - \eta_E \eta_к)}. \tag{8}$$

The product $\eta_E\ \eta_K$ is approximately 0.025; accordingly, if the order of accuracy required is not too high, this value can be disregarded with respect to unity.

During determination of ketones and esters in each other's presence it is desirable that their absorption bands should be resolved on a spectrogram. The ketone and ester bands are resolved by the IKS-11 apparatus fitted with an NaCl prism for a spectral slit width of 9 cm^{-1}, when the optical density of one band is not more than twice that of the other. In addition, the optical density should not be more than 0.3. This ratio of the optical densities was checked by us on synthetic mixtures, and also by means of spectrograms of oxidized paraffins. In Fig. 2 are given the resolution of ketone and ester bands for mixtures of oxidized paraffins, as well as the values of their optical densities.

In the case of the analysis of highly-oxidized paraffins, when appreciable amounts of acids are formed, for increasing the experimental accuracy of the determination of ketones and esters it is best to remove the acids or to convert them into salts. The carbonyl band is strongly shifted to the lower frequency side (down to 1560 cm^{-1}) in the spectra of the carboxylic acid salts. This opens up the further possibility of determining ketones and acids in the presence of acids, since, by converting the latter into salts by neutralization with alkali, it is then possible to eliminate mutual superposition of the carbonyl bands almost completely. The analysis can then be carried out as described above.

TABLE 3

Concentration in mole/liter, according to the Infrared Spectra

Ketones	Esters
0.45	0.26
0.47	0.24
0.50	0.29

Various methods can be used according to the nature of the test material:

1. For the analysis of samples of oxidized high-molecular weight paraffins, it is best to neutralize and partially remove the acids by converting them into their salts. This is carried out by dissolving a test sample in a mixture of water and alcohol (1 : 1) and neutralizing it with alcoholic KOH to the phenolein endpoint. A known volume of cyclohexane, heptane, or other suitable solvent is then added to the contents of the flask; the flask is strongly shaken and sealed with a ground glass stopper; after separation of the layers, a few mls of the upper layer is pipetted out. After drying for

TABLE 4

Oxidation product	Acid No. of oxidate	Determination, N	conc'n. per infrared spectra in moles/1	
			ketones	esters
Oxidate No. 1				
a) Neutralized with KOH	33	1	0,49	0,293
b) Saponified with KOH by boiling for 2 hr; extract. with petroleum ether		2	0,47	
c) Partially titrated to acid number 10.7		3	0,48	0,288
Oxidate No. 2				
Oxidized paraffin	110	1	0,193	0,92
		2	0,190	0,89
Oxidate No. 3	23	1	0,17	0,170
		2	0,20	0,20

TABLE 5

Composition of mixture	ketone conct., in moles/liter		ester conct., in moles/liter		Solvent
	wt. of synth. mix. taken	as found by infra-red	wt. of synth. mix. taken	as found by infra-red	
Methyl stearate Methyl ethyl ketone	0,0652	0,0634	0,0615	0,0615	Cyclohexane
Esters from $C_{10} - C_{16}$ acids and C_{13} alcohols	0,0288	0,0284	0,0201	0,0209	Cyclohexane
Esters of $C_{14} - C_{16}$ acids and C_{13} alcohols Methyl ethyl ketone + $C_{14} - C_{16}$ acids	ketone 0.0310 acid 0.0199	—	0,0467	0,0464	Cyclohexane
Esters of $C_{14}-C_{16}$ acid and C_{13} alcohols. Ketones (mixture) mol.wt 249.	0,01620	0,01625	0,00790	0,00745	CCl_4

TABLE 6

Oxidate	ketones, in moles/1.		esters, in moles/1.	
	ketones, moles/1	by chem. analy.	ketones moles/1	by chem. analy.
Oxidate No. 1, oxidized paraffin	0,48	0,50	0,290	0,290
Oxidate No. 1, partially neutralized to acid number 10.6	0,46	0,48		
Oxidate No. 1, neutralized	0,42	0,435		
Oxidate No. 2, a. No = 10.7			1,67	1,40
Oxidate No. 3			1,47	1,28
Oxidate No. 4			0,456	0,44
Oxidate No. 5			1,21	0,92

a short time with a small amount of $MgSO_4$, the spectrum of the solution obtained is registered and the ketone content determined by means of formula (4). During extraction of the neutralized sample with cyclohexane some of the salts formed may be taken up in the cyclohexane layer; this, however, as indicated above, should not affect the accuracy of the method. A basic source of error could be the transfer of the ketones or other carbonyl-containing compound into the aqueous-alcohol phase. All the same, during analysis of oxidized paraffin, these errors amount to less than 0.5%, since after a supplementary extraction of the aqueous-alcohol phase with cyclohexane, no ketones are found in the latter. Table 3 shows the reproducibility for determination of ketones and esters by means of their infrared spectra after removal of acids, followed by extraction with cyclohexane; the test material was oxidized paraffin with an acid number of 33.

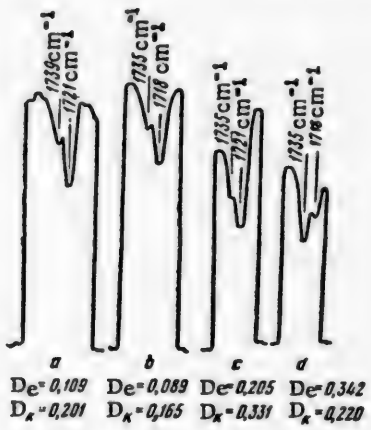

Fig. 2. Absorption bands of the > C = O group of ketones and esters in oxidized paraffins (IKS-11 apparatus).

2. In those cases where extraction is undesirable for some reason or other, the following procedure is adopted: a sample of the test mixture is dissolved in a few milliliters of absolute alcohol with gentle warming, and the solution neutralized with alcoholic KOH. The alcohol is then removed by evaporation under vacuum, or by heating; the residue is dissolved in a known volume of CCl_4, after which the spectra are registered. A large part of the acid salts remains in the precipitate. This sequence of operations, can, of course, only be followed when one can be sure that no ketones or esters will be lost.

For the analysis of solid oxidized paraffins, the following method is also suitable: an aliquot of the oxidized paraffin is neutralized with 0.1 N alcoholic KOH in an aqueous-alcohol (1 : 1) mixture with preliminary warming until the whole sample has dissolved. The precipitate is filtered off and dried in air, together with the filter paper. An aliquot of this precipitate is dissolved in carbon tetrachloride or some other suitable solvent, and the spectra of the carbonyl group resistered; the concentrations of ketones and esters are then calculated.

Table 4 contains results which characterize the reproducibility of this procedure. For oxidate No. 1 results are given for the concentration of ketones and esters when the test material was treated in three different ways with alkali: 1) complete removal of acids; 2) partial removal of acids until an acid value of 10.6 was obtained; 3) saponification by boiling in normal KOH for 2 hours on a water bath.

In those cases where a rapid but not-so-accurate determination is required of the concentration of ketones and acids, and where removal of acids is not resorted to, use can be made of the absorption coefficients which have been corrected for mutual superposition of the bands.

Table 5 contains results for the analysis of synthetic mixtures; experimental accuracy amounts to ± 3-6 %.

We have also carried out a large number of determinations of ketones by the hydroxylamine-pyridine method [13] for control purposes. The results obtained by both methods are in satisfactory agreement with each other. The small, systematic difference between the results obtained by the hydroxylamine method and those obtained by the infrared method, can, in our opinion, be related to the presence of high-molecular weight ketones which do not react completely with hydroxylamine.

The generally accepted method of estimating esters in an oxidized sample is their saponification by heating with alkali followed by titration with acid. The values for ester concentration given in Table 6 were determined by this method.

The ester values found by saponification are higher than those found by the infrared method. There seem to be no systematic regularities in these deviations.

In conclusion we should like to express our thanks to N. K. Man'kovskii for his gift of samples of oxidized paraffins and acids for the work.

SUMMARY

It has been shown that it is possible to determine ketones and esters in mixtures of oxidation products and paraffins on the basis of the absorption spectra of the >C=O bond.

Absorption coefficients and band contours have been measured for individual materials, and for mixtures of carbonyl-containing materials, by means of the IKS-11 apparatus. The effect of the shift in the frequencies of the components of the mixtures on the extinction coefficients of the absorption bands of the mixtures has been established.

The values of the corrections to be applied to the absorption coefficients, when ketones, esters, and acids are all present together, have been determined. Methods are described for removing the acids so that the accuracy with which the ketones and esters can be determined is increased.

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COLOR REACTIONS OF NITROINDANEDIONE

COMMUNICATION II. REACTIONS WITH INDOLES AND CARBAZOLE*

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2-Nitroindanedione-1,3 [$C_6H_4=(CO)_2=CH \cdot NO_2$] gives a series of color reactions with organic compounds [1], which can be used for the qualitative detection of these compounds. Of these reactions, those with pyrroles are particularly valuable. Pyrroles give red or orange colors with nitroindanedione both in aqueous and in alcoholic and acetic acid solutions; the color appears without application of heat. Heating usually enhances the sensitivity of the reaction. Thus, pyrrole gives a red color with nitroindanedione which can be detected at a dilution of 1 : 200,000, while on heating it can be detected at a dilution of 1 : 3,333,000. With N-methylpyrrole a red color can be observed at a dilution of 1 : 333,000 in the cold, while on heating the color can be observed at a dilution of 1 : 10,000,000.

In this connection it appeared interesting to investigate the behavior of compounds containing the pyrrole ring condensed with other rings. The reactions of nitroindanedione with indoles and carbazole form the subject of the work described here.

Colors Given with Nitroindanedione (in Alcoholic, Acetic Acid, or Aqueous Solutions)

Test material	Color of the solution observed	Limiting dilution at which a color can still be observed	
		Without heating	After heating
Indole	Red	1 : 333,000	1 : 333,000
N-Methylindole	Red	1 : 125,000	1 : 250,000
2-Methylindole	Orange to violet	1 : 100,000	1 : 100,000
3-Methylindole (skatole)	Orange	No color	1 : 50,000
7-Methylindole	Red	1 : 500,000	1 : 5,000,000
2,3-Dimethylindole	Orange to violet	On heating in glacial acetic acid	
2,3-Diphenylindole	Orange to red	On heating in glacial acetic acid	
Carbazole	Orange	No color	1 : 20,000

Indole and its homologs give very intense colors with nitroindanedione, these colors frequently appearing without applying heat. When a drop of a dilute alcohol solution of indole is added to a saturated aqueous solution of nitroindanedione, a red color appears almost immediately. The limiting dilution at which this red color can still be observed is 1 : 333,000. Heating, in the case of very dilute indole solutions, speeds up the appearance of the color somewhat, but the reaction sensitivity does not increase. When the indole solutions are not very dilute, a red precipitate is obtained, particularly on heating.

Of the indole homologs tested, 7-methylindole (see Table) exhibits the highest reaction sensitivity with nitroindanedione. A red color is observed; at the limiting dilution the color is, however, orange. The reactions

*For Communication I see Bull. Acad. Sci. Latvian SSSR, No. 10 (87), 143 (1954).

of N-methylindole, and of 2-methyl- and 3-methylindole (skatole) with the reagent are less sensitive.

When an aqueous or alcoholic solution of nitroindanedione is heated with heteroauxin (3-indoleacetic acid), then only after 15 minutes does a weak orange color appear. A solution in glacial acetic acid, however, on boiling, gives a red color after one minute. The reaction has a low sensitivity; it is possible that heteroauxine itself does not give a color, but that a color is given by its decomposition products (e.g. products formed by decarboxylation) which may be formed on boiling.

2-3-Dimethylindole initially gives a greenish color which gradually changes to violet, when it is reacted with an aqueous solution of nitroindanedione. On heating, the color becomes an intense red; further prolonged boiling changes the color to brown and a red precipitate formed. In alcoholic solution a greenish-violet color is observed at first, but this changes to red. In glacial acetic acid, on heating, an orange color is very rapidly observed. The sensitivity is low.

2,3-Diphenylindole does not give a color with nitroindanedione in aqueous solution, but in alcoholic and in glacial acetic acid, on heating, an orange color is first observed which changes over to red. The reaction sensitivity is low.

Some samples of petroleum contain porphyrins [2]. Pyrroles and indoles would also be expected to be present in petroleum in addition to porphyrins. It was actually found that petroleum gives colors which are characteristic of indoles and pyrroles when tested with nitroindanedione.

When one or two drops of Bakinskii petroleum is diluted with alcohol or glacial acetic acid, and some nitroindanedione added, and the mixture then allowed to stand for some time or heated for a few minutes, a red, red-violet, or violet color appears. The same effect can be obtained by shaking Bakinskii petroleum with alcohol or glacial acetic acid and adding nitroindanedione to the filtrate.

Carbazole, on heating with nitroindanedione in alcoholic solution, gives an orange color. The limiting dilution is 20,000.

It has been shown previously [3] that 2-bromo-2-nitroindanedione-1,3 also gives a number of color reactions with pyrroles, indoles, and carbazole; the highest reaction sensitivity is exhibited by carbazole while the least sensitive reactions are those with indoles and pyrroles. The reaction between bromonitroindanedione with tryptophane is very characteristic; nitroindanedione, however, does not give a color with tryptophane. Thus, both reagents can supplement each other.

The reaction is carried out by adding nitroindanedione, either in the solid form or in solution, to a test solution in alcohol, glacial acetic acid, or water, and shaking the whole. When indoles (and pyrroles) are present, a color appears rapidly; this color is usually red or violet-red; at high dilutions the color is orange. When no color is observed, the solution is heated. The appearance of a color only after heating for some time indicates a very low concentration of indoles or pyrroles, or indicates the presence of indoles substituted in the 2 and 3 positions, or the presence of carbazole.

SUMMARY

2-Nitroindanedione-1,3 gives characteristic colors in alcoholic, acetic, or aqueous solutions with indole, its homologs, and carbazole. With indoles the color usually develops without application of heat.

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*Original Russian pagination. See C. B. Translation.

DETERMINATION OF MIXTURES OF XYLENE AND ETHYL-BENZENE ISOMERS

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Chemical methods of analyzing the isomeric composition of technical xylene, despite the appearance of spectrographic methods, are still fairly widely used, since they ensure satisfactory accuracy, and do not require complicated apparatus. The method based on sulfonation of xylene followed by separation of the sulfonic acids or their salts [1-4], gives large errors, particularly during determination of the contents of o-xylene and ethylbenzene. Determination of xylene isomers by oxidizing them into the corresponding dicarboxylic acids, and determination of ethylbenzene by its oxidation to benzoic acid [5,6] lead to losses which are difficult to assess during oxidation, particularly during separation of the acids; as a consequence, it has been suggested that this mixture of acids should be analyzed by an X-ray method [7]. Some authors have converted the mixture of xylene isomers into the trinitro derivatives with subsequent determination of the latter [8-13]. This method permits determination of meta- and para-xylene, and total o-xylene and ethylbenzene with reasonable accuracy.

The technique which we have developed permits quantitative determination of all three xylene isomers and ethylbenzene; it is based on nitration of the mixture of xylene isomers, and determination of the trinitro derivatives according to the method published earlier [14], coupled with quantitative separation by efficient fractionation of o-xylene which boils 5.3° higher than m-xylene, which is the isomer which has the boiling point nearest to it [15].

Determination of o-xylene.* The original technical xylene consisted of a mixture of the three isomeric xylenes and ethylbenzene, and did not contain more than 1% non-aromatic hydrocarbons;** it was fractionated for removal of the o-xylene, using a column of 33 theoretical plates and a reflux ratio of not less than 15 : 1. The fractions boiling up to 139.5° were almost free of o-xylene; all the latter remained in the residue. The o-xylene content of the bottoms was determined from the temperature of crystallization, using the fusion diagram for the system o-xylene—m-xylene; on the basis of this result, the content of the o-xylene in the original xylene was then determined.

TABLE 1

Determination of o-Xylene

o-xylene taken		o-xylene found		Relative error, in %
in g	in %	in g	in %	
30.0	15.0	29.4	14.7	−2
30.0	15.0	28.8	14.4	−4
50.0	25.0	50.0	25.0	0
60.0	30.0	58.5	29.3	−2.3

We were of the opinion that the impurity most likely remaining with the o-xylene in the bottoms would be m-xylene, since the latter has the boiling point which is nearest to that of o-xylene. In view of the comparatively

*N. E. Khromova-Borisova and N. G. Borzova took part in the experimental work.

**When the test sample contained an appreciable amount of non-aromatic hydrocarbons, they were removed beforehand by azeotropic distillation with methanol [17].

small volume of the bottoms during analysis of technical xylene, the error arising out of the possible presence of small amounts of other isomers, which is a consequence of such an assumption, is insignificant.

Results are given in Table 1 for the determination, by the method described, of o-xylene in synthetic other mixtures containing the other isomers.

Determination of m-Xylene, p-Xylene, and Ethylbenzene. The fraction of xylene boiling up to 139.5°, and which was free from o-xylene, was nitrated to give trinitrotoluenes in two stages; in the first stage the xylene was nitrated to the dinitro state, while the second stage consisted of converting the dinitro compounds to the trinitro derivatives.

First Stage: 5 g of xylene was placed in a nitration flask provided with a stirrer, a reflux condenser with a groundglass joint, a dropping funnel, and a thermometer.

While the xylene was stirred and the temperature kept at not more than 40° on a water bath, a nitrating mixture of the following composition was added dropwise to the contents of the flask: 61-62% sulfuric acid, 20-25% nitric acid, and 13-14% of water; the nitrating activity factor was 75-76.* The amount of nitrating mixture taken was such that the amount of nitric acid present was 10% in excess of that theoretically necessary.

When all the nitrating acid had been added, the temperature was gradually increased to 90-95°, and kept at this temperature for one hour, the mixture being stirred continuously. The contents of the nitration flask were then allowed to cool to room temperature; the nitrated product was isolated from the waste acid and subjected to further nitration.

Second Stage. To the fused dinitro product heated to 60-70° was added with stirring a second mixture of acids containing 80-81% sulfuric acid, 13-14% of nitric acid, and 5-6% of water; the nitrating activity factor in this case was 88-89. The amount of nitrating mixture taken was such that the amount of nitric acid present was 65% in excess of the theoretical amount (for nitration from dinitro to trinitro). When all the nitrating mixture had been added, the final mixture was kept at 100° for 30 minutes, and for 2 hours at 120°, the mixture being agitated continuously. The contents of the nitration flask were then cooled to room temperature and poured into 5-6 times their volume of cold water. After settling, the diluted acid was decanted through a tared Nutsch filter with a No. 3 and No. 4 sintered glass disc. The trinitro product remaining in the flask was washed 3 times with cold water and twice with hot (60-70°) water, using 100 ml portions each time. The wash water was decanted through the same filter. When washing with hot water, the contents of the flask were cooled again to 20-25° before decanting off the wash water. All the trinitro product was transferred onto the filter by means of the last lot of wash water; the trinitro product was squeezed free of water (not too strongly, to avoid loss of the oily part) and dried to constant weight at 60°. Filter plus trinitro product were then weighed and the total yield of the trinitro derivatives of m-, p-xylene, and ethylbenzene determined.

The nitrated ethylbenzene, which is considerably more soluble in alcohol than the trinitro derivatives of m- and p-xylene [16], was removed by washing the nitrated product on the filter with ethanol in 10 ml portions, the product being thoroughly mixed with the alcohol on the filter and the wash alcohol then sucked off. Completion of the washing process was established by the absence of oily drops of the nitroproduct on evaporating a few drops of the wash alcohol on a watch glass. 7 washings were usually enough.

The filter, together with the nitro product which had been treated as described above with alcohol was then dried to constant weight at 60°; the total yield of trinitrometa- and trinitroparaxylene was then determined. The proportions of these two were established by means of setting points and the appropriate fusion diagram [14].

The oily product soluble in alcohol contains, in addition to trinitroethylbenzene, some incompletely nitrated nitration products of m- and p-xylene; the amounts of these products, under the nitration conditions used, amounted to — according to our results — about 2% of the weight of trinitrometaxylene and about 10% of the weight of trinitroparaxylene. These amounts were taken into account during determination of the amounts of trinitroethylbenzene (see the example given).

* The nitrating activity factor "F" is calculated by means of the formula [19]:

$$F = \frac{S}{1 - \frac{N}{140}}$$

where S is the sulfuric acid content of the mixture in %, N is the nitric acid content of the mixture in %.

On the basis of the analytical results obtained for the nitration products, the proportions of the various isomers in the xylene taken for nitration were calculated, by making use of the experimental coefficients which we established for the yields of the trinitro products during nitration under identical conditions of the individual xylene isomers, and of synthetic mixtures of these isomers in different proportions. These coefficients, which were established experimentally, are:

for m-xylene – 1.95 (for a m-xylene content of the mixture up to 80%)
for m-xylene – 2.0 (for a m-xylene content of 80-90%)
for m-xylene – 2.1 (for a m-xylene content greater than 90%)
for p-xylene – 1.55
for ethylbenzene – 1.65

Example. Determination of the composition of xylene by the nitration method.

During nitration of 5 g of xylene the following were obtained:

Oily trinitro product	– 9.10 g
Weight of non-oily trinitroxylene after washing	– 6.50 g
Weight of "xylene oil," removed with alcohol by alcohol washing	– 2.60 g

The setting point of the non-oily trinitroxylene was 170.0° which corresponds to a composition of 75% trinitro-metaxylene and 25% trinitroparaxylene

Weight of trinitrometaxylene	6.50 · 0.75 = 4.88 g
Weight of trinitroparaxylene	6.50 · 0.25 = 1.62 g
Weight of incompletely nitrated products	
During nitration of m-xylene:	4.88 · 0.02 = 0.1 g
During nitration of p-xylene:	1.62 · 0.1 = 0.16 g
	Total 0.26 g
Weight of trinitroethylbenzene	2.60 g - 0.25 g = 2.35 g

On the basis of the experimental coefficients for the yield of trinitroproducts during nitration, we can now calculate the composition of the original xylene:

Amount of m-xylene in the original xylene taken for nitration 4.88/1.95 = 2.5 g, or 50%.

Amount of p-xylene 1.62/1.65 = 1.05 g or 21%.

Amount of ethylbenzene 2.34/1.65 = 1.42 g or 28.5% = approximately 29%.

Results of the analysis of several synthetic mixtures of m-, and p-xylene and ethylbenzene by the method described above are given in Table 2.

TABLE 2

Analysis of Synthetic Mixtures of m- and p-Xylene and Ethylbenzene

Taken, in g			Found, in g			Relative error, in %		
m-xylene	p-xylene	Ethyl-benzene	m-xylene	p-xylene	Ethyl-benzene	m-xylene	p-xylene	Ethyl-benzene
3.50	1.50	–	3.50	1.55	–	0	+3.3	–
			3.62	1.48	–	+2.9	–0.7	–
3.90	0.60	0.50	3.90	0.63	0.55	0	+5.0	+10
			3.95	0.64	0.53	+1.3	+6.7	+6
1.0	1.50	2.50	0.94	1.55	2.65	–6.0	+3.3	+6
			0.92	1.52	2.70	–8.0	+1.3	+8
–	2.50	2.50	–	2.40	2.60	–	–4.0	+4
				2.48	2.45	–	–0.6	–2
3.75	–	1.25	3.73	–	1.27	–0.3	–	+2
			3.79	–	1.25	+1.3	–	0

Some of the xylene samples analyzed by the method described were also analyzed spectrophotometrically.* Both methods gave results which agreed with each other satisfactorily (Table 3).

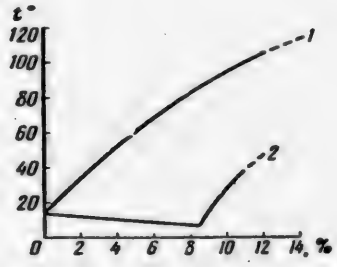
TABLE 3

Comparisons of the Results of the Nitration and Spectrophotometric Methods of Analyzing Xylene

By the nitration method, in %				By the spectrophotometric method, in %			
o-xylene	m-xylene	p-xylene	ethyl-benzene	o-xylene	m-xylene	p-xylene	ethylbenzene
21	37	18	24	20	36	19	25
–	47	23	30	–	43	24	33
–	13	18	69	–	11	19	70
17.5	47	19	17.5	17	45	19	19

The method described gives satisfactory results during the analysis of typical samples of technical xylene consisting of mixtures of all the xylene isomers and ethylbenzene. This method can also be used for the analysis of mixtures of m- and p-xylene in any proportions, and for the determination of other xylene isomers present as impurities in m-xylene. In the case of analysis of experimental mixtures of isomers containing a predominating amount of ethylbenzene (50-80%) during nitration very oily, products, which are difficult to filter, are obtained. In order to avoid this, samples with ethylbenzene contents in excess of 40% can be nitrated, by adding a known amount of pure m-xylene to such samples prior to nitration, and then taking the amount of m-xylene added into account during the final calculation.

For the analysis of xylene fractions containing 85% and more of ethylbenzene, the remaining components being m- and p-xylenes,** the method described is not suitable, since the trinitro-products obtained are liquid in form and contain very small amounts of crystals which are difficult to filter from the liquid phase. Addition of m-xylene in order to increase the amount of solid phase in the trinitro products is not applicable either, since in the given instance, it leads to large errors during the determination.



Relation between the temperature of incipient crystallization and the content of trinitrometa- and trinitro-paraxylene in trinitroethylbenzene: 1) Trinftrometaxylene; 2) trinitro-paraxylene.

For such fractions we have developed another analytical technique: the p-xylene content was determined by means of the temperature of incipient crystallization; the m-xylene content was determined by the nitration method, and the ethylbenzene content was determined by difference.

Determination of p-Xylene. To 3-5 g of test sample was added p-xylene in sufficient amount to bring the crystallization point down below 40°. The temperature of incipient crystallization ot this mixture was then determined; from the fusion diagram for the system p-xylene – ethylbenzene [18] the amount of p-xylene in the mixture was then determined. After subtracting the amount of p-xylene added in the first instance, the content of p-xylene in the original xylene was determined. The experimental error in determining p-xylene, when using a low-temperature thermometer with 0.5 divisions, is about 5% absolute.

Addition of p-xylene is necessary to avoid too low temperatures and to prevent overcooling of the system.

* The spectrophotometric analysis was carried out in the physical laboratory of the Leningrad Sci. Research Institute of the Ministry of the Oil Industry by A. N. Aleksandrov.

** o-Xylene is absent from these fractions since it is readily removed quantitatively by efficient fractional distillation.

The presence of m-xylene in the test sample does not interfere with determination of p-xylene by the method described, since in this concentration range the depression of the temperature caused by the m-xylene is almost the same as that caused by ethylbenzene [18].

Determination of m-Xylene. A separate aliquot of test sample (5 g) was nitrated to the trinitro product, which was a mixture of trinitroethylbenzene, trinitrometaxylene, and trinitroparaxylene. Nitration and washing were carried out as described above.

The washed nitro-product was dried at 60° to constant weight in the same vessel as that used for washing. The dried product was heated until it was completely liquid when it was poured into a test tube; the latter was placed in an apparatus for determining setting points, the apparatus being heated to a temperature slightly higher then the expected incipient temperature of crystallization. The apparatus was cooled slowly and the temperature at which the contents of the tube started to become turbid (initial separation of solid phase) noted.

The trinitrometaxylene content of the nitro-product was determined by means of a diagram* (Fig. 1, Curve 1) constructed on the basis of the relationship which we established between the temperature of incipient crystallization of the nitro-product and its content in trinitrometaxylene. Then, using the coefficient established experimentally for the yield of trinitrometaxylene during nitration — equal, in the given instance to 1.95 — the m-xylene content of the test sample was calculated.

Example. During nitration of 5 g of a sample of ethylbenzene containing m-xylene, 8.1 g of trinitro-derivative with an initial temperature of crystallization of 96° was obtained; this corresponds to a content of trinitrometaxylene of 10%.

The amount of trinitrometaxylene 0.1 · 8.1 = 0.81 g.

The amount of m-xylene in the original sample = 0.81/1.95 = 0.415 g or 8.3%.

The presence of up to 8.5% of trinitroparaxylene in the nitro-product does not affect the temperature at which crystals of trinitrometaxylene separate out, as the result of the formation of melts of trinitroparaxylene and trinitroethylbenzene with a low temperature of incipient crystallization and an eutectic at a content of 8.5% of trinitroparaxylene (Fig. 1, Curve 2). For trinitroparaxylene contents in excess of 8.5%, it crystallizes from the melt (as the component in excess when compared with the composition of the eutectic) at the same temperatures as those at which it crystallizes from the same melt of trinitrometaxylene (see Fig. 1, Curve 2); accordingly trinitrometaxylene cannot be determined on the basis of the temperature of incipient crystallization of the nitro-product. In this case, in order to decrease the concentration of the p-xylene in the test sample, pure ethylbenzene should be added in known amounts to the sample; the synthetic mixture thus obtained should then be analyzed as described above, and the amount of ethylbenzene added originally taken into account during the calculation.

TABLE 4

Determination of Small Amounts of m-Xylene in Ethylbenzene

m-Xylene taken		m-Xylene found		Relative error, in %
in g	in %	in g	in %	
0.2	2.0	0.163	1.63	−8.0
0.18	3.6	0.17	3.4	−5.6
0.5	5.0	0.51	5.1	+ 2.0
0.5	5.0	0.52	5.2	+ 4.0
0.4	8.0	0.415	8.3	+ 3.8
0.8	8.0	0.73	7.3	−8.8
0.8	8.0	0.76	7.6	−7.0
1.0	10.0	0.91	9.1	−9.0

*The setting point of pure trinitroethylbenzene is 37° [20]. Technical dinitroethylbenzene is liquid at room temperature. The technical product obtained by nitration of ethylbenzene to the trinitro derivative, as we showed experimentally, contained 4-5% of dinitroethylbenzene, and this depressed the setting point to 14-15°.

Results for the determination of the m-xylene content of synthetic mixtures by means of the method described are given in Table 4.

In view of the low absolute values of the m-xylene being determined, the relative error is fairly considerable, but the absolute error does not exceed 1%.

SUMMARY

1. A method is suggested for the analysis of technical xylene in which all the xylene isomers are determined, together with the amount of ethylbenzene present; the method consists of fractional distillation for removal of o-xylene, followed by nitration in conjunction with phase analysis for the determination of m-xylene, p-xylene, and ethylbenzene.

2. A method has been developed for determination of the isomeric composition of xylenes and ethylbenzene in mixtures with a high content of ethylbenzene (upwards of 85%).

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CHROMATOGRAPHIC SEPARATION OF RHENIUM AND TUNGSTEN

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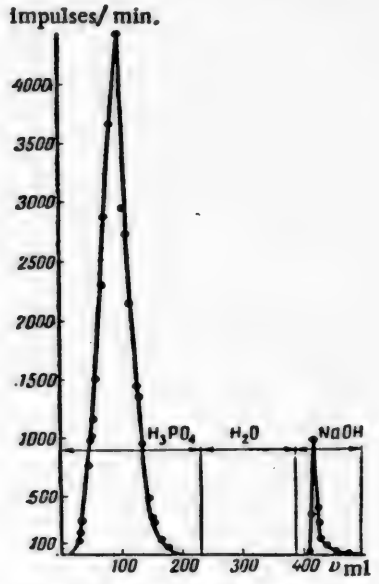
Rhenium and molybdenum exhibit a large difference in their capacity to be absorbed on the anion exchange resin EDE-10 from phosphoric acid media [1]. Sexivalent molybdenum forms a heteropoly compound with phosphoric acid, in which the molybdenum is located in the complex anion which is readily sorbed by the anion exchange resin; rhenium in the septivalent state does not form such compounds, but passes into the filtrate on washing the column with 2 M H_3PO_4. Tungsten also tends to form a heteropoly compound with phosphoric acid, which is similar to those formed between molybdenum and phosphoric acid [2-3]; this permits separation of rhenium from tungsten.



Chromatographic separation of weighable amounts of rhenium and tungsten.

Rhenium is used for coating tungsten wire in filaments [4], and also forms alloys with tungsten which are used in new technical fields. Separation of this pair of elements is therefore of importance for their subsequent determination.

Rhenium was separated from tungsten under dynamic conditions on a column 12 cm long and 6 mm in diameter filled with anion exchange resin EDE-10 in the phosphate form; the particle size of the resin was 100-150 mesh. Synthetic mixtures of W : Re = 1000 : 1; 1 : 1; and 1 : 400 were used for the work. The mixtures were made up from weighable and tracer portions of these elements. The tracers used were the radioisotopes W^{185} and Re^{186}, whose purity was checked radiometrically. 0.1-0.2 ml of the mixture of tungsten and rhenium in the form of sodium tungstate and sodium perrhenate respectively, was introduced into the upper part of the column, and the rhenium eluted with 2 M H_3PO_4. The elution process was controlled by measuring the activity of the Re^{185} in the eluate, and by the color reaction with $SnCl_2$ and KSCN. When all the rhenium had been eluted off the column, the latter was washed with water; the tungsten was then eluted from the column with 10% NaOH. That all the tungsten had been eluted was checked by the absence of activity in the last portions of eluate, and by a negative reaction for tungsten with thiocyanate.

On the basis of the results obtained for the activities of the various portions of eluates, and the changes in intensity of the color of these eluates, an elution curve was constructed for rhenium and tungsten. The separation of tungsten and rhenium for a ratio of one to the other of 1 : 1 is shown in Fig. 1. The curves are similar in character for the other ratios of the two metals. Completeness of elution of Re^{186} and W^{185} was established by summing the activities of the individual portions of eluate, while quantitative determination of weighable amounts of rhenium and tungsten was carried out by means of nitron acetate for rhenium [5], and photometrically, using the thiocyanate reaction for tungsten [6].

W taken		Re taken		Ratio	W found		Re found	
in mg	in impulses/ / minute	in mg	in impulses/ / minute	W : Re*	in mg	in impulses/ / minute	in mg	in impulses/ / minute
	2500	4		1 : 400		2561	4.09	
8		8		1 : 1	8.2		8.07	
4			23040	1000 : 1	4.12			23140

*The ratios by weight of W : Re were calculated on the basis of the specific activity of the radioisotopes Re^{188} and W^{185}.

The results given in the Table show that rhenium is removed satisfactorily from tungsten by anion exchange.

SUMMARY

A method has been developed for separating rhenium from tungsten on the anion exhcnage resin EDE-10 using 2 M H_3PO_4. Separation of the elements is based on differences in their behavior towards phosphoric acid which forms complex anions with tungsten only; these anions are strongly held by the active groups of the resin.

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THE REACTION OF URANIUM WITH FERRON (7-IODO-8-HYDROXY-QUINOLINE-5-SULFONIC ACID)

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Sexivalent uranium gives with ferron an intense brown color at a pH of 5 in an urotropine buffer. The sensitivity of the reaction when carried out in a volume of 2 ml is equal to 10 γ / ml (limiting dilution 1 : 10^5). No reaction occurs at the same pH in an acetate buffer. Maximum color intensity is observed at pH 4.5-5.5. Using the isomolar series method of Ostromyslenskii - Zhob (at 520 and 360 mμ) it was established that uranium and ferron interact in the molar proportions of 1 : 2 (Fig. 1).

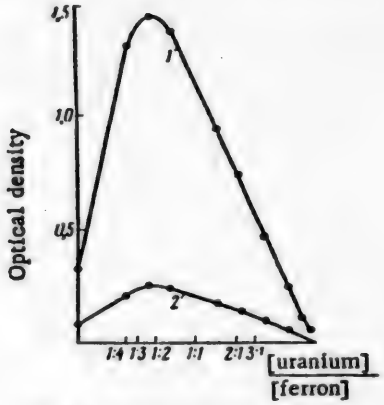

Fig. 1. Determination of the composition of the compound formed between uranium and ferron, using the isomolar series method. pH 5 (urotropine), total concentration of uranium and ferron $1.7 \cdot 10^{-3}$ mole/liter. Reference cell – water. 1) At 360 mμ; 2) at 520 mμ.

During the photometric determination of aluminum [1-2], and during the precipitation of thorium [3] with ferron in an acetate buffer, no formation of the brown color was observed in the presence of uranium.

From the point of view of selectivity the reaction of uranium with ferron is of no great interest. The reagent reacts with trivalent iron [2, 4]. The absorption curves of ferron and of the compounds formed between this reagent and uranium, aluminum, and iron [2] respectively, are shown in Fig. 1. Ferron solution in strongly acidic or alkaline mediahas a light absorption maximum at 360 mμ, while at pH 4-5 the maximum lies at 340 and 430 mμ (Fig. 2). The compound of ferron with uranium also shows a maximum at 360 mμ. This curve is similar to the absorption curve for ferron in alkaline media, but differs from the latter by its appreciable absorption at 430-600 mμ. The same absorption maximum at 360 mμ is also observed in the case of the compounds formed between ferron and trivalent iron and aluminum. The fact that the position of the light absorption maximum is the same for the reagent itself in alkaline media, and for the compounds which it forms in more acid media (pH 5), leads one to conclude, according to Kuznetsov's hypothesis [5], that inner molecular dissociation occurs here. It is of interest to note that the intensity of this light-absorption band is directly proportional to the number of ferron groups in the molecule, while the mean coefficient E_{360} calculated per mole of ferron is approximately 2300. The occurrence of light absorption in the visible may be related to the chromophoric action of sexivalent uranium [6-7]. This conclusion is confirmed by a consideration of the absorption curves of the compounds formed between ferron and aluminum or iron. The aluminum ion does not exhibit a chromophoric action, while the ferric ion does possess this property. Accordingly, the aluminum compound hardly absorbs at all in the region above 430 mμ, while the iron compound absorbs light in the visible more strongly than uranium, and has an additional maximum at 600 mμ.

Thus, comparison of the absorption curves leads one to conclude that during formation of the compounds of ferron with iron and uranium respectively, the two mechanisms of color formation noted by Kuznetsov [5,6] occur

together. The nature of the changes in the curves indicates that iron exerts a stronger chromophoric action than uranium.

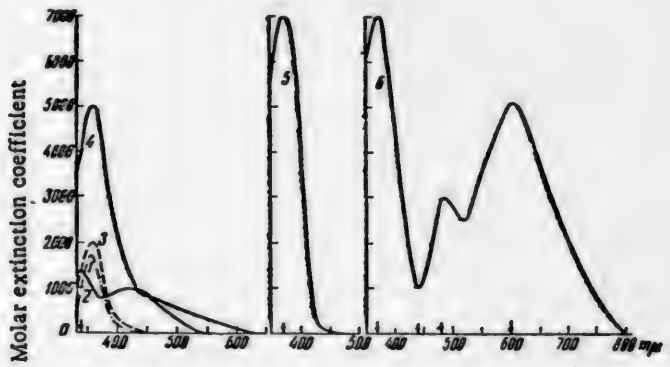

Fig. 2. Absorption curves: 1) Ferron at pH 0; 2) ferron at pH 5; 3) ferron at pH 8-13; 4) compound of uranium with ferron at pH 5 (urotropine); 5) aluminum compound at pH 5 (acetate buffer); 6) iron compound at pH 5 (acetate buffer). Reference cell – water.

SUMMARY

A color reaction of uranium with ferron is described. On the basis of a comparison of the absorption curves, the mechanism of the reaction is considered.

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DETECTION OF MAGNESIUM IONS BY MEANS OF N-ARYLQUINOCYANINE DYES

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A large number of reagents are known for the qualitative detection of magnesium; these reagents interact with magnesium ions to give colored precipitates or colored solutions [1-6].

We have tested N-arylquinocyanine dyes for detecting magnesium. The syntheses of these dyes have been described in the literature [7-9].

All the trimethine quinocyanine dyes with a symmetrical structure (with similar hetero residues at each end of the polymethine chain) which we tested proved to be very sensitive reagents for magnesium ions.

All the dyes studied, both symmetrical and unsymmetrical in structure, are almost insoluble in water, but are readily soluble in ethanol, forming intensely colored solutions; we used their 0.01-0.02% alcoholic solutions. In acid and neutral solutions of magnesium salts, on addition of alcoholic solutions of dyes of symmetrical and unsymmetrical structure, no changes were observed in the colors of the solutions or of the colored precipitates as compared with a "blank". When, however, in the same cases, to 1 ml of a solution of magnesium salt, slightly colored by an alcoholic solution of a trimethinequinocyanine dye with a symmetrical structure, two or three drops of NaOH or KOH solution was added, and intensely colored precipitate was formed.

It must be pointed out that in the case of appreciable concentrations of magnesium in solution, it is best to use, as tests showed, a 0.1 N alkali solution; while for low concentrations the alkali strength should be 2 N solution.

The colored precipitates formed do not decompose on heating the solutions to the boiling point.

Addition of alkali to solutions of magnesium salts, to which an alcoholic solution of a dye with an unsymmetrical structure has been added beforehand, led to the precipitation, for the most part, of colorless magnesium hydroxide.

The table contains results obtained during the study of the interaction between magnesium hydroxide and several symmetrical trimethinequinocyanine dyes.

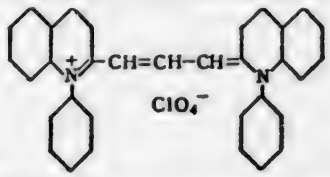
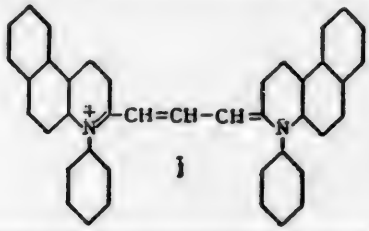
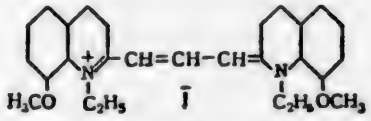
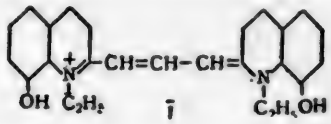
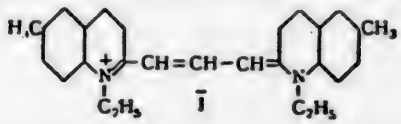
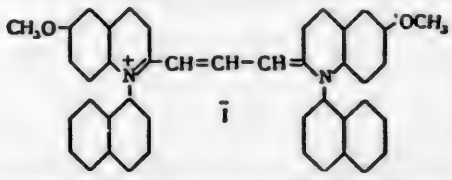
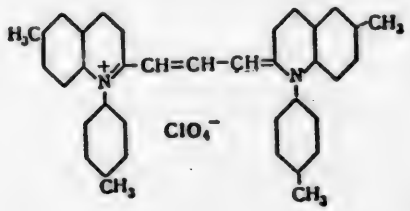
K^+, Na^+, NH_4^+, Ba^{2+}, Sr^{2+}, Ca^{2+} ions do not give colored precipitates, and do not change the color of alkaline solutions of the dyes. For a ratio of magnesium to each of these ions of 1 : 500, there is no appreciable drop in the sensitivity of the reactions for all seven dyes. There is no drop in reaction sensitivity at a ratio of Mg^{2+} : NH_4^+ of 1 : 100. The dye bis-(1-phenyl-5,6-benzoquinoline-2)-trimethinecyanine iodide is particularly sensitive (0.1 γ/ml); the sensitivity of this dye for magnesium ions is considerably higher than that of many known reagents for magnesium (titan yellow, magneson, quinalizarin, triozenes, and hydroxytriazenes, etc.).

Most ions of the fourth and fifth analytical groups interfere with detection of magnesium by means of trimethinequinocyanine dyes, since in alkaline media, hydroxides and basic salts are precipitated which mask the reaction for magnesium; such elements must therefore be removed before detecting magnesium.

For removing interfering ions, the latter are precipitated as sulfides by means of Na_2S under strictly controlled pH values of the test solution.

Procedure for Detecting Magnesium Ions. When the test solution contains free acid, the solution must be neutralized beforehand by adding approximately 0.1 N NaOH dropwise until the appearance of a slight turbidity

Interaction of Trimethinequinocyanine Dyes with Magnesium Ions in an Alkali Solution

Dye	Color of		Limit of identification, in γ/ml. Limiting dilution
	Alkaline solution of dye	precipitate formed	
	Violet	Red light blue	1 : 500 000
	Light-blue	Dark-blue	0,1 1 : 10 000 000
	Rose	Red-violet	2 1 : 500 000
	Violet	Red-blue	2 1 : 500 000
	Violet	Red	5 1 : 200 000
	Blue	Red-violet	1 1 : 1 000 000
	Violet	Red	1 1 : 10 000 00

which does not disappear; this turbidity is then destroyed by addition of a few drops of 0.1 N HCl.

To 0.5-1 ml of test solution prepared in this way is added 1-2 ml of borate buffer solution (pH 7.60-7.80) and the heavy metals precipitated as their sulfides by dropwise addition of 0.5 N Na_2S. After addition of each drop of sulfide, the contents of the tube are mixed and tests carried out for excess S^{2-}. This is carried out by dipping a capillary pipet for some time in the test solution, and then touching a piece of filter paper moistened beforehand with 1-2 drops of 0.5 N $SbCl_5$ with the tip of the pipet. When precipitation of group III, IV, and V elements is complete, and the minimum amount of Na_2S is present in solution, a clearly discernible orange ring is observed around the tip of the capillary. When it is certain that precipitation of the sulfides is complete, the contents of the test tube are filtered through a close filter paper and the test for magnesium carried out.

2-3 drops of a 0.01-0.02% alcoholic solution of one of the dyes indicated in the table is then added to the filtrate; this is followed by 2-3 drops of 2 N NaOH and the whole mixed; precipitation of a colored precipitate is observed against a white background. The appearance of such a precipitate indicates the presence of magnesium ions.

SUMMARY

It has been shown that some trimethinequinocyanine dyes with a symmetrical structure are highly sensitive reagents for magnesium ions. A method has been developed for detecting magnesium in solutions containing ions of all the five analytical groups, by means of trimethinequinocyanine dyes.

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DETERMINATION OF ALCOHOLS AND PHENOLS PRESENT AS IMPURITIES IN ORGANOSILICON COMPOUNDS CONTAINING ETHOXY-, METHOXY-, AND PHENOXY-GROUPS

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In order to determine alcohols photometrically we have made use of a reaction which we have described in the literature [1]; this reaction is based on the capacity of alcohols to dissolve $Fe[Fe(SCN)_6]$ with the production of a red color. In addition, we have also suggested a method of determining alcohols present as impurities; this is based on the capacity of alcohols to dissolve the dye methyl violet with formation of a solution with a violet color, while organosilicon compounds containing alkoxy-groups do not dissolve this reagent. $Fe[Fe(SCN)_6]$ was used as the dry powder; the latter was prepared by dissolving 10 g of potassium thiocyanate and 10 g of ferric chloride in separate portions, in 50 ml of absolute methanol.

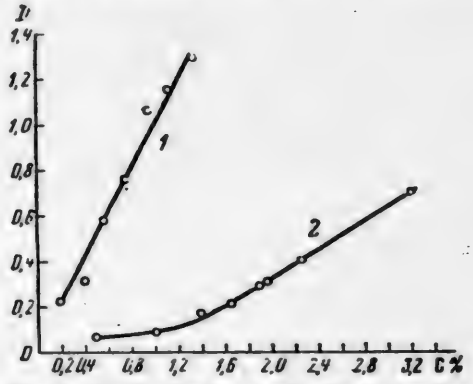

Fig. 1. Calibration curves for determination of alcohol: 1) With $Fe[Fe(SCN)_6]$; 2) with methyl violet.

Solutions of ethanol in tetraethoxysilane were prepared for constructing calibration curves (Fig. 1). To 5-10 ml of these solutions contained in 15-20 ml conical flasks was added about 0.1 g of $Fe[Fe(SCN)_6]$ or methyl violet. The flasks were sealed with stoppers and the contents shaken and then allowed to stand for 20-40 minutes; the solutions were finally centrifuged and the optical density measured on a Pulfrich photometer.

In order to determine the alcohol content of a given sample of tetraethoxysilane or some other organosilicon compound containing ethoxy groups, a known volume of test material was subjected to the same treatment as that used for preparing standards for the calibration curve. The absolute experimental error is 0.01-0.02%, while the relative error is about 1%. The method permits determination of alcohol contents up to the limit of 1.5% when using $Fe[Fe(SCN)_6]$, and from 1.4 to 4-5% when using methyl violet.

The method involving methyl violet has also been tried out with methanol.

Phenol has to be determined in the water extract removed from phenoxysilanes and other organosilicon compounds which are insoluble in water [2]. A ground-up sample of tetraphenoxysilane or phenyltriphenoxysilane

containing phenol as impurity was placed in a conical flask and 3-5 ml of water added; the mixture was shaken thoroughly and then centrifuged. To the centrifugate was added 3 drops of 10% $FeCl_3$ solution, or 3 drops of 10% cuprammonium solution. Under these conditions the phenol solution acquired a violet or green color. The optical density of the solutions obtained was finally measured on a Pulfrich photometer.

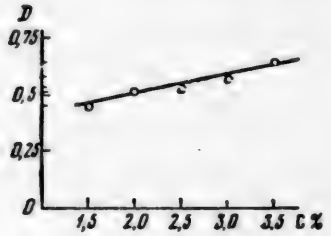

Fig. 2. Calibration curve for determination of phenol with $FeCl_3$.

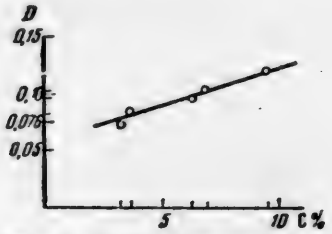

Fig. 3. Calibration curve for determination of phenol by means of the cuprammonium complex.

In order to construct calibration curves (Figs. 2 and 3) aqueous solutions of phenol were prepared. When $FeCl_3$ is used, the limit of identification is 0.05% of phenol, while when the cuprammonium complex is used the limit of identification is 0.15%. The relative error in both cases amounts to 0.7-1.4%.

SUMMARY

Photometric methods are described for the determination of ethanol and methanol present as impurities in organosilicon compounds; a method is also described for determination of phenol as an impurity in the same compounds.

Received January 9, 1957

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*Original Russian pagination. See C. B. Translation.

SEPARATION OF IRON AND COPPER CATIONS BY PAPER CHROMATOGRAPHY IN THE PRESENCE OF LARGE AMOUNTS OF CARBOHYDRATES

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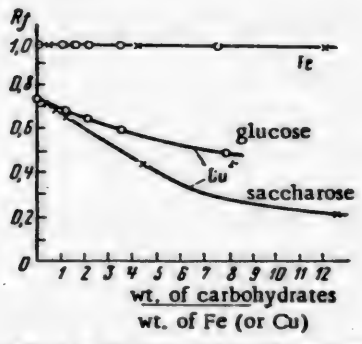
There are well-developed methods in existence at the moment for the paper chromatographic separation of various inorganic compounds, and of a number of organic compounds: carbohydrates, amono acids, etc. [1, 2]. There is, however, practically no published information on the effect of large amounts of organic materials on the chromatographic behavior of inorganic compounds; this is a problem that one often meets in the analysis of foodstuffs.

Of particular interest to us was the study of the effect of carbohydrates (saccharose, glucose) on the chromatographic separation of Fe^{3+} and Cu^{2+}

Amount of carbohydrate, in mg	Ratio carbohydrate / Fe^{3+}	Ratio carbohydrate / Cu^{2+}	R_f Fe^{3+}	R_f Cu^{2+}	Amount of carbohydrate, in mg	Ratio carbohydrate / Fe^{3+}	Ratio carbohydrate / Cu^{2+}	R_f Fe^{3+}	R_f Cu^{2+}
Glucose					Saccharose				
0	0	0	0,98	0,75	0,3	0,22	0,315	0,98	0,75
1,05	0,79	1,11	0,98	0,68	1,1	0,82	1,16	0,98	0,66
2,0	1,49	2,11	0,98	0,66	4,1	3,06	4,32	0,98	0,43
3,3	2,46	3,48	0,98	0,60	12,0	8,2	12,6	0,98	0,23
7,5	5,60	7,90	0,98	0,49					

The behavior of ferric and cupric ions during chromatographic separation in media free from carbohydrates has has been thoroughly studied [3], while the R_f values of cupric and ferric ions in various solvents are known. One of the carbohydrates which we studied – glucose – has reducing properties [4], while the other – saccharose – does not possess these properties [5].



Effect of glucose and saccharose on the R_f values of ferric and cupric cations.

Ferric and cupric ions were separated by ascending chromatography [2] on paper from the Volodarskii factory. The solvent used was a mixture of acetone – hydrochloric acid – water in the proportions 87 : 8 : 5. During separation of ferric and cupric ions by means of mixtures of different composition, i.e., with mixtures of acetone, acid, and water in the proportions 87 : 10 : 3, 87 : 7 : 6, and 87 : 5 : 8, the results obtained were not so well-defined. The R_f value found for iron was 0.38, while that for copper was 0.75; these results are in good agreement with the published values [3]. The chromatograms were developed by spraying with ammonium sulfide [2].

Chromatographic separation of ferric and cupric ions in the presence of carbohydrates was carried out as follows: a drop of an iron solution was placed on a sheet of chromatographic paper and the spot dried out; after drying, a drop of a copper solution was placed on the same place and the drying process repeated; finally a drop of carbohydrate solution of a given concentration was placed on the same spot. The sheet was dried again and a chromatogram run using the same solvent mixture as that indicated above. Replicate chromatograms were run for each test concentration of glucose and saccharose.

The presence of glucose and saccharose in large amounts (Table 1) has no effect on the mobility of ferric ions. Within the limits of experimental error, in all cases $R_f = 0.98$. Thus, Fe^{3+} does not interact with glucose and saccharose (iron was used as a solution of $FeCl_3$).

Glucose and saccharose, however, strongly affect the mobility of cupric ions. In the presence of these carbohydrates the migration rate of the copper drops significantly, the drop being greater the higher the carbohydrate concentration (Fig. 1).

Saccharose exhibits a stronger slowing-up effect than glucose.

We should like to point out that both in the absence of carbohydrates, and in their presence, in all tests, the chromatographic zones for the ferric and cupric ions were quite clearly defined after development with ammonium sulfide. It is probable that in the presence of glucose and saccharose, there is a change in the value of the partition coefficient for the cupric ion between the mobile and immobile solvents, while the partition coefficient for ferric ions, presumably, remains unchanged.

The experiments described above show that it is possible to use the paper chromatographic method for separating Fe^{3+} and Cu^{2+} cations, and for determining them in solutions of saccharose and glucose. Identification of the cations on the basis of the R_f value is only possible in the case of Fe^{3+}. In the case of copper it is essential to bear in mind the slowing action of the carbohydrates.

SUMMARY

It has been shown that large amounts of glucose and saccharose do not affect the mobility of trivalent iron cations, but decrease the mobility of copper ions to a considerable extent. Saccharose decreases the mobility to a greater extent than glucose.

Received April 24, 1957

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DETECTION OF URANYL IONS

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A method which has been published in the literature [1] for the detection of uranyl ions in the presence of appreciable amounts of foreign ions (Fe^{3+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Ti^{4+}, Zr^{4+}, Th^{4+}, VO_3^-, MoO_4^{2-}, etc.), on checking has proved to be unreliable: when potassium ferrocyanide was added to the solution, in many cases, there appeared colored precipitates which prevented one from deciding conclusively whether uranium was present or not. Other methods [2, 3] have not attained practical importance.

After several preliminary tests we succeeded in developing a method for detecting uranyl ions in solution containing Mg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Ce^{3+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Be^{2+}, Ti^{4+}, Zr^{4+}, Th^{4+}, VO_3^-, MoO_4^{2-}, WO_4^{2-}.

To 2-3 ml of the test solution is added an equal volume of a 10% solution of Complexon III in order to keep most of the metal ions in solution; concentrated ammonia solution is then added until the solution has an ammoniacal odor (if, on addition of ammonia an appreciable amount of precipitate is not formed, it is recommended that some beryllium be added in the form of a solution of one of its salts in order to serve as a collector); the mixture is next heated to the boiling point at which temperature it is kept for two to three minutes; it is finally filtered. The precipitate on the filter, which may contain, in addition to ammonium diuranate, the hydroxides of beryllium, titanium, antimony and some manganese, is washed with hot water until a completely colorless wash liquor is obtained. The precipitate on the filter is treated with a hot 10% solution of sodium carbonate or ammonium carbonate (2-3 ml), the filtrate being passed two or three times through the same filter in order to get more complete solution. During this treatment uranium passes into the filtrate. To one portion of the filtrate is added a drop of a 30% solution of hydrogen peroxide. The rapid appearance of a yellow color indicates the presence of uranium in solution (when sodium carbonate is used for treating the precipitate, chromium may partly dissolve but the chromate color does not appear immediately; uranium can be detected in the presence of chromium at a ratio of uranium to chromium of 1 : 1000); the use of ammonium carbonate at this stage in the presence of large amounts of chromium gives a reaction which is completely reliable.

To another portion of filtrate is added some solid sodium carbonate, and 2-3 drops of potassium ferrocyanide, and about 0.5 ml of 2N HNO_3 added carefully along the wall of the vessel; in the presence of uranium a brown ring is formed at the surface of contact between the sodium carbonate solution and the acid.

The method permits detection of 10^{-5} g/ml of uranium (limiting dilution 1 : 100, 000) in the presence of large amounts of other elements.

SUMMARY

A method has been developed for detecting uranyl ions in a solution containing Mg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Ce^{3+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Be^{2+}, Ti^{4+}, Zr^{4+}, Th^{4+}, VO_3^-, MoO_4^{2-}, WO_4^{2-}. The method permits detection of 10^{-5} g/ml of uranium (limiting dilution 1 : 100,000) in the presence of large amounts of other elements.

Received April 25, 1957

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CHRONICLE

THE CONFERENCE HELD AT IVANOVO ON METHODS OF STUDYING COMPLEX FORMATION IN SOLUTION

A conference was held at Ivanovo from the eighteenth to the twenty-first of February which was devoted to discussions of the methods used for studying complex formation in solution. More than 200 delegates attended the conference, among them scientific workers from Moscow, Leningrad, Kiev, Kazan, Kishinev, Kharkov, Alma-Ata and other cities. Thirty reports were read at the seven sessions. The conference was opened by Academician I. I. Chemiaev. His opening speech was followed by I. V. Tananaev's report on "Methods of determining the composition of compounds formed in solution," and also the report by V. N. Tolmachev on "Some limitation of the isomolar series method." In his report, A. K. Babko set forth the principles of the methods of titrating and taking logarithms used for determining composition. V. I. Kuznetsov drew attention, in his paper, to the necessity of studying the changes in chemical reactivity of groups in organic compounds which enter into the composition of complex compounds.

K. B. Iatsimirskii's report was devoted to the complicated, and hitherto comparatively little studied hydrolytic polymerization of metal ions in solution. The report of I. I. Alekseeva (in conjunction with K. B. Iatsimirskii) was devoted to polymeric compounds of molybdenum. In the discussion that followed, the arbitrary character of the term "polymerization" was noted, as well as the necessity for studying the structure of polymers, and taking into account the role of the anions.

A. K. Babko examined experimental methods for determining the dissociation constants of complex groups in solution. N. P. Komar' gave a critical review of methods of calculating successive instability constants (Bjerrum, Leden, etc.) and noted the necessity of making wider use of the method of least squares for calculating the instability constants. A. K. Babko and others who participated in the discussion, pointed out the possibilities of using simpler methods including graphical methods. N. P. Komar' noted the appearance of published papers dealing critically with Bjerrum's concepts of the existence of step-like complex formation in solution.

Other reports which proved of considerable interest were those of A. P. Zozuli (in conjunction with V. M. Peshkova) on the use of the partition method for studying the stability constants of complex thorium compounds, and the report by B. D. Berezin on the study of the solubility of metal phthalocyanine complexes. A new technique for carrying out spectrophotometric studies of complex compounds was recommended by L. P. Adamovich. In his report, A. A. Grinberg gave results on the formation of solution of hitherto unknown complex compounds of divalent palladium, with a coordination number greater than 4.

K. B. Iatsimirskii (together with V. D. Korableva) discussed the use of the theory of the crystalline field for studying certain complexes. The study of complex formation by means of dielectric constants and polarization was the subject of the report by I. A. Sheka and Z. A. Sheka (together with N. E. Kriss). T. N. Sumarovka dealt with the use of the cryoscopic method. V. F. Toropova discussed the possibilities of the polarographic method for studying complex compounds in solution.

At the final session a number of papers were read which dealt with studies of the effect of the solvent on complex formation in solution. Some examples of equilibrium studies in non-aqueous solutions were given in reports by Ia. A. Fialkov, A. V. Ablov, Ia. I. Tur'ian and in communications by B. N. Tolmachev, A. M. Golub, and A. G. Muftalov.

V. P. Vasil'ev made an attempt to calculate the constants for formation of aquo-complexes.

V. A. Mikhailov

CONFERENCE ON POLAROGRAPHIC METHODS OF ANALYSIS

(21-23 January 1958, Kishinev)

The conference on polarographic methods was convened at the instigation of the Analytical Chemistry Department of Kishinev University, the Analytical Chemistry Laboratory of the Moldavian Branch of the USSR Academy of Sciences, and the Kishinev Section of the Mendeleev Society. Scientific workers from Moscow and Dnepropetrovsk participated in the conference in addition to workers from Kishinev. 18 reports were read at the conference, 12 of which were given by workers in Kishinev scientific-research institutions, while the other 6 were given by scientists from Moscow and Dnepropetrovsk.

Several reports dealt with theoretical questions of polarographic analysis (S. I. Siniakova, Ia. I. Tur'ian, A. N. Pushniak, M. B. Bardin, Iu. S. Lialikov, A. A. Gabovich, A. M. Gabovich, and V. M. Bobrinskii).

A number of reports were devoted to the practical application of polarographic analysis and to amperometric titration (N. A. Ezerskaia, V. S. Temianko, Iu. I. Usatenko, V. L. Reznik, E. F. Danilenko and F. M. Tiuliupa; B. V. Lipis, S. Ia. Raik, F. P. Vaintraub, R. M. Novik).

All the reports were heard with great interest and led to lively discussion.

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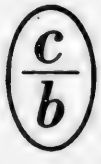

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